

**A TEXT-BOOK OF
INORGANIC CHEMISTRY
VOLUME VII., PART II.**

IN ELEVEN VOLUMES. Medium Svo. Cloth. Prices are net Postage extra.

A TEXT-BOOK OF INORGANIC CHEMISTRY.

EDITED BY

J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C.,

Carnegie Gold Medallist.

- | | | |
|--------------|---|---|
| VOLUME I. | { | An Introduction to Modern Inorganic Chemistry. By J. NEWTON FRIEND, D.Sc. (B'ham), Ph.D. (Wurz); H. F. V. LITTLE, B.Sc. (Lond.), A.R.C.S., Chief Chemist to Thorium, Ltd.; W. E. S. TURNER, D.Sc. (Lond.). The Inert Gases. By H. V. A. BRISCOE, D.Sc. (Lond.), A.R.C.S. |
| VOLUME II. | { | The Alkali Metals and their Congeners. By A. JAMIESON WALKER, Ph.D. (Heid), B.A. (Q.U.B.), F.I.C. Pp. i-xxvi + 379. 20s.
PART I. The Alkaline Earth Metals. By MAY SYBIL BURR (née LESLIE), D.Sc. (Leeds). Pp. i-xxvi + 346. 20s. |
| VOLUME III. | { | PART II. Beryllium and its Congeners. By JOSHUA C. GREGORY, B.Sc. (Lond.), F.I.C., and MAY SYBIL BURR, D.Sc. (Leeds). Pp. i-xxvi + 320. 18s. |
| VOLUME IV. | { | Aluminium and its Congeners, including the Rare Earth Metals. By H. F. V. LITTLE, B.Sc. (Lond.), A.R.C.S., Chief Chemist to Thorium, Ltd. Second Edition. Pp. xxviii + 485. 18s. |
| VOLUME V. | { | Carbon and its Allies. By R. M. CAVEN, D.Sc. (Lond.), F.I.C. Second Edition. Pp. i-xxi + 468. 18s. |
| VOLUME VI. | { | PART I. Nitrogen. By E. B. R. PRIDEAUX, M.A., D.Sc., F.I.C., and H. LAMBOURNE, M.A., M.Sc., F.I.C. Pp. i-xxviii + 242. 18s.
PART II. Phosphorus and its Congeners. By E. B. R. PRIDEAUX, M.A., D.Sc., F.I.C., W. E. THORNEycroft, B.Sc., and B. D. SHAW, B.Sc., Ph.D. In Preparation.
PART III. Vanadium, Niobium, and Tantalum. By SYDNEY MARKS, M.Sc., A.I.C. Pp. i-xxvi + 222. 18s. |
| VOLUME VII. | { | PART I. Oxygen. By J. NEWTON FRIEND, D.Sc., and DOUGLAS F. TWISS, D.Sc., F.I.C. Pp. i-xxvi + 370. 18s.
PART II. Sulphur, Selenium, and Tellurium. By REECE H. VALLANCE, M.Sc., F.I.C., DOUGLAS F. TWISS, D.Sc., F.I.C., and Miss A. R. RUSSELL, B.Sc., A.I.C. Pp. i-xxviii + 420.
PART III. Chromium and its Congeners. By REECE H. VALLANCE, M.Sc., A.I.C., and ARTHUR A. ELDRIDGE, B.Sc., F.I.C. Pp. i-xxvi + 380. 18s. |
| VOLUME VIII. | { | The Halogens and their Allies. By GEOFFREY MARTIN, D.Sc., Ph.D., and ERNEST A. DANCATER, B.Sc. (Lond.). Second Edition. |
| VOLUME IX. | { | PART I. Cobalt, Nickel, and the Elements of the Platinum Group. By J. NEWTON FRIEND, D.Sc. (B'ham). Second Edition. Pp. i-xxvi + 367. 18s.
PART II. Iron and its Compounds. By J. NEWTON FRIEND, D.Sc. Pp. i-xxvi + 265. 18s. |
| VOLUME X. | { | The Metal-Ammines, with a General Introduction to the Theory of Complex Inorganic Substances. By Miss M. M. J. SUTHERLAND, D.Sc., F.I.C. Pp. i-xxvi + 260. 18s. |
| VOLUME XI. | { | Organometallic Compounds.
PART I. Derivatives of the Elements of Groups I to IV. By ARCHIBALD E. GODDARD, M.Sc., A.I.C., and DOROTHY GODDARD, M.Sc. Pp. i-xxviii + 418. 25s.
PART II. Derivatives of Arsenic. By ARCHIBALD E. GODDARD, M.Sc., A.I.C. Pp. i-xxviii + 605. 42s.
PART III. Derivatives of the Elements of Groups V to VIII (excluding Arsenic). By ARCHIBALD E. GODDARD, M.Sc., A.I.C. In Preparation. |

LONDON: CHARLES GRIFFIN & CO., LTD., 42 DRURY LANE, W.C.2.

A TEXT-BOOK OF INORGANIC CHEMISTRY.

EDITED BY
J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C.,
CARNEGIE GOLD MEDALLIST.

VOLUME VII., PART II.

SULPHUR, SELENIUM, AND TELLURIUM.

BY
REECE H. VALLANCE, M.Sc. (B'ham), F.I.C.,
DOUGLAS F. TWISS, D.Sc. (B'ham), F.I.C.,
AND
MISS ANNIE R. RUSSELL, B.Sc. (Glas.), A.I.C.



LONDON:
CHARLES GRIFFIN & COMPANY, LIMITED,
42 DRURY LANE, W.C.2.

1931.

Printed in Great Britain by
NAILL & Co., LTD., EDINBURGH

GENERAL INTRODUCTION TO THE SERIES.

DURING the past few years the civilised world has begun to realise the advantages accruing to scientific research, with the result that an ever-increasing amount of time and thought is being devoted to various branches of science.

No study has progressed more rapidly than chemistry. This science may be divided roughly into several branches : namely, Organic, Physical, Inorganic, and Analytical Chemistry. It is impossible to write any single text-book which shall contain within its two covers a thorough treatment of any one of these branches, owing to the vast amount of information that has been accumulated. The need is rather for a series of text-books dealing more or less comprehensively with each branch of chemistry. This has already been attempted by enterprising firms, so far as physical and analytical chemistry are concerned ; and the present series is designed to meet the needs of inorganic chemists. One great advantage of this procedure lies in the fact that our knowledge of the different sections of science does not progress at the same rate. Consequently, as soon as any particular part advances out of proportion to others, the volume dealing with that section may be easily revised or rewritten as occasion requires.

Some method of classifying the elements for treatment in this way is clearly essential, and we have adopted the Periodic Classification with slight alterations, devoting a whole volume to the consideration of the elements in each vertical column, as will be evident from a glance at the scheme in the Frontispiece.

In the first volume, in addition to a detailed account of the elements of Group O, the general principles of Inorganic Chemistry are discussed. Particular pains have been taken in the selection of material for this volume, and an attempt has been made to present to the reader a clear account of the principles upon which our knowledge of modern Inorganic Chemistry is based.

At the outset it may be well to explain that it was not intended to write a complete text-book of Physical Chemistry. Numerous excellent works have already been devoted to this subject, and a volume on such lines would scarcely serve as a suitable introduction to this series. Whilst Physical Chemistry deals with the general principles applied to all branches of theoretical chemistry, our aim has been to emphasise their application to Inorganic Chemistry, with which branch of the subject this series of text-books is exclusively concerned. To this end practically all the illustrations to the laws and principles discussed in Volume I. deal with inorganic substances.

Again, there are many subjects, such as the methods employed in the accurate determination of atomic weights, which are not generally regarded as forming part of Physical Chemistry. Yet these are

subjects of supreme importance to the student of Inorganic Chemistry and are accordingly included in the Introduction.

Hydrogen and the ammonium salts are dealt with in Volume II., along with the elements of Group I. The position of the rare earth metals in the Periodic Classification has for many years been a source of difficulty. They have all been included in Volume IV., along with the elements of Group III., as this was found to be the most suitable place for them.

Many alloys and compounds have an equal claim to be considered in two or more volumes of this series, but this would entail unnecessary duplication. For example, alloys of copper and tin might be dealt with in Volumes II. and V. respectively. Similarly, certain double salts—such, for example, as ferrous ammonium sulphate—might very logically be included in Volume II. under ammonium, and in Volume IX. under iron. As a general rule this difficulty has been overcome by treating complex substances, containing two or more metals or bases, in that volume dealing with the metal or base which belongs to the highest group of the Periodic Table. For example, the alloys of copper and tin are detailed in Volume V. along with tin, since copper occurs earlier, namely, in Volume II. Similarly, ferrous ammonium sulphate is discussed in Volume IX. under iron, and not under ammonium in Volume II. The ferro-cyanides are likewise dealt with in Volume IX.

But even with this arrangement it has not always been found easy to adopt a perfectly logical line of treatment. For example, in the chromates and permanganates the chromium and manganese function as part of the acid radicals and are analogous to sulphur and chlorine in sulphates and perchlorates; so that they should be treated in the volume dealing with the metal acting as base, namely, in the case of potassium permanganate, under potassium in Volume II. But the alkali permanganates possess such close analogies with one another that separate treatment of these salts hardly seems desirable. They are therefore considered in Volume VIII.

Numerous other little irregularities of a like nature occur, but it is hoped that, by means of carefully compiled indexes and frequent cross-referencing to the texts of the separate volumes, the student will experience no difficulty in finding the information he requires.

Particular care has been taken with the sections dealing with the atomic weights of the elements in question. The figures given are not necessarily those to be found in the original memoirs, but have been recalculated, except where otherwise stated, using the following fundamental values:

Hydrogen	=	1.00762.	Oxygen	=	16.000.
Sodium	=	22.996.	Sulphur	=	32.065.
Potassium	=	39.100.	Fluorine	=	19.015.
Silver	=	107.880.	Chlorine	=	35.457.
Carbon	=	12.008.	Bromine	=	79.916.
Nitrogen	=	14.008.	Iodine	=	126.920.

By adopting this method it is easy to compare directly the results of earlier investigators with those of more recent date, and moreover it renders the data for the different elements strictly comparable throughout the whole series.

Our aim has not been to make the volumes absolutely exhaustive,

GENERAL INTRODUCTION TO THE SERIES.

ix

as this would render them unnecessarily bulky and expensive; rather has it been to contribute concise and suggestive accounts of the various topics, and to append numerous references to the leading works and memoirs dealing with the same. Every effort has been made to render these references accurate and reliable, and it is hoped that they will prove a useful feature of the series. The more important abbreviations, which are substantially the same as those adopted by the Chemical Society, are detailed in the subjoined lists, pp. xvii-xix.

The addition of the *Table of Dates of Issue of Journals* (pp. xxi-xxviii) will, it is hoped, enhance the value of this series. It is believed that the list is perfectly correct, as all the figures have been checked against the volumes on the shelves of the library of the Chemical Society by Mr. F. W. Clifford and his staff. To these gentlemen the Editor and the Authors desire to express their deep indebtedness.

In order that the series shall attain the maximum utility, it is necessary to arrange for a certain amount of uniformity throughout, and this involves the suppression of the personality of the individual author to a corresponding extent for the sake of the common welfare. It is at once my duty and my pleasure to express my sincere appreciation of the kind and ready manner in which the authors have accommodated themselves to this task, which, without their hearty co-operation, could never have been successful. Finally, I wish to acknowledge the unfailing courtesy of the publishers, Messrs. Charles Griffin & Co., who have done everything in their power to render the work straightforward and easy.

J. NEWTON FRIEND.

January 1931.

PREFACE.

OF the three elements dealt with in this volume, two are of comparatively recent discovery, the existence of tellurium being recognised only in 1798 and that of selenium about twenty years later. Sulphur has been known from antiquity, and there is evidence that its inflammable and fumigating properties were made use of 3000 years ago; by the alchemists it was regarded as the "principle of inflammability" and included as one of their *tria prima*; to the phlogistonists it was a compound of phlogiston and sulphuric acid; Lavoisier, in 1777, however, showed it to be a true element, and to-day it is undoubtedly recognised as one of the most important.

The part now played in chemical industry by sulphur and its wide variety of compounds scarcely needs emphasis. The astonishing increase in the production of sulphur and sulphuric acid during the last two decades, made possible by the discovery of the vast deposits of sulphur in Louisiana, is itself indicative of widespread applications. Many of the compounds of sulphur are notable for possessing valuable properties, and their use extends into almost every branch of modern industry; their chemical investigation has contributed much to the advancement of science and to the amenities of domestic life. Probably in no direction has sulphur more widely and directly influenced the general public than in connection with methods of transport, which have been revolutionised by the introduction of sulphur-vulcanised rubber as a wear-resisting, shock-absorbing material for the equipment of wheels of motor vehicles.

Selenium and tellurium are generally considered rare elements and are not found in abundance; each, however, has a claim to special interest. The peculiar electrical properties of selenium appeal especially to the physical chemist, but the compounds of this element are of growing importance, especially in their application to the glass industry. Both selenium and tellurium offer attractive fields for research. In the case of tellurium, owing to what had been considered an erroneous value for the atomic weight, the very considerable amount of work done in the past has been too much confined to one direction; interest in the chemistry of tellurium appears now to be widening, however.

PREFACE.

OF the three elements dealt with in this volume, two are of comparatively recent discovery, the existence of tellurium being recognised only in 1798 and that of selenium about twenty years later. Sulphur has been known from antiquity, and there is evidence that its inflammable and fumigating properties were made use of 3000 years ago; by the alchemists it was regarded as the "principle of inflammability" and included as one of their *tria prima*; to the phlogistonists it was a compound of phlogiston and sulphuric acid; Lavoisier, in 1777, however, showed it to be a true element, and to-day it is undoubtedly recognised as one of the most important.

The part now played in chemical industry by sulphur and its wide variety of compounds scarcely needs emphasis. The astonishing increase in the production of sulphur and sulphuric acid during the last two decades, made possible by the discovery of the vast deposits of sulphur in Louisiana, is itself indicative of widespread applications. Many of the compounds of sulphur are notable for possessing valuable properties, and their use extends into almost every branch of modern industry; their chemical investigation has contributed much to the advancement of science and to the amenities of domestic life. Probably in no direction has sulphur more widely and directly influenced the general public than in connection with methods of transport, which have been revolutionised by the introduction of sulphur-vulcanised rubber as a wear-resisting, shock-absorbing material for the equipment of wheels of motor vehicles.

Selenium and tellurium are generally considered rare elements and are not found in abundance; each, however, has a claim to special interest. The peculiar electrical properties of selenium appeal especially to the physical chemist, but the compounds of this element are of growing importance, especially in their application to the glass industry. Both selenium and tellurium offer attractive fields for research. In the case of tellurium, owing to what had been considered an erroneous value for the atomic weight, the very considerable amount of work done in the past has been too much confined to one direction; interest in the chemistry of tellurium appears now to be widening, however.

SULPHUR, SELENIUM, AND TELLURIUM.

Every effort has been made to render the present work of a high standard of usefulness and worthy of the Series.

The Authors desire to thank the Editor, Dr J. Newton Friend, for his kindly help and advice throughout the production of the work.

REECE H. VALLANCE.

D. F. TWISS.

A. R. RUSSELL.

January 1931.

CONTENTS.

	PAGE
THE PERIODIC TABLE (<i>Frontispiece</i>)	iv
GENERAL INTRODUCTION TO THE SERIES	vii
PREFACE	xi
LIST OF ABBREVIATIONS	xvii
TABLE OF DATES OF ISSUE OF JOURNALS	xxi

CHAPTER I. General Characteristics of the Elements of Group VI., Subdivision B	8
---	---

CHAPTER II. Sulphur	8
-------------------------------	---

Occurrence, Extraction, Refining, Applications—The Allotropy of Sulphur :
Changes in the Vaporous State, Allotropy in the Liquid State, Allotropy
in the Solid State, Crystalline Forms of Sulphur, Amorphous Sulphur—
Colloidal Sulphur—General Physical Properties of Sulphur—Chemical
Properties—Valency—Atomic Weight—Detection and Estimation.

CHAPTER III. Compounds of Sulphur	46
---	----

GENERAL.

SULPHUR AND HYDROGEN :—Hydrogen Sulphide : Occurrence, History, Forma-
tion and Preparation, Purification, Physical Properties, Chemical Properties,
Physiological Action, The Metallic Sulphides, Detection and Estimation
—The Polysulphides : Polysulphides of the Metals, Hydrogen Poly-
sulphides.

HALIDES AND OXYHALIDES OF SULPHUR :—Fluorides, Chlorides, Sulphur
Bromide, Sulphur and Iodine, Oxyfluorides, Oxychlorides, Thionyl Bromide.

SULPHUR AND OXYGEN :—General—Sulphur Dioxide : Occurrence, Preparation,
Physical Properties, Chemical Properties, Physiological Action, Applications,
Detection and Estimation, Formula and Constitution—Sulphurous Acid :
Formation, Properties, Detection and Estimation, The Sulphites, Consti-
tution—Sulphur Trioxide : Historical, Formation and Preparation,
Physical Properties, Chemical Properties, Constitution—Pyrosulphuric
Acid : Preparation, Physical Properties, Chemical Properties, Constitution,
Estimation, Pyrosulphates—Sulphuric Acid : Occurrence, Early History,
Formation, Manufacture, The "Lead Chamber Process," The Contact Process,
Physical Properties, Hydrates, Chemical Properties, Applications, The
Sulphates, Molecular Weight and Constitution, Detection and Estimation
—Persulphuric Anhydride—Perdisulphuric Acid and the Perdisulphates
—Permonosulphuric Acid (Caro's Acid)—Amidopermonosulphuric Acid
(Hydroxylamine-sulphonic Acid)—Thiosulphuric Acid and the Thio-
sulphates—The Polythionic Acids and Polythionates—Sulphur Sesquioxide
—Hydrosulphurous Acid and the Hydrosulphites.

SULPHUR AND NITROGEN :—Nitrogen Sulphides, Sulphammonium, Hexasulphamide, Chloro- and Bromo-sulphides, Thiazyl Salts—Amides of the Sulphur Oxy-acids—Sulphonic Acids—Sulphur Compounds of Hydroxylamine and Hydrazine.

SULPHUR AND CARBON :—Carbon Subsulphide, Carbon Monosulphide—Carbon Disulphide and its Derivatives, Reduction Products of Carbon Disulphide, Thio-acids and -salts Derived from Carbon Disulphide—Carbon Oxy-sulphide—Halogen Derivatives of Sulphur and Carbon—Amino-derivatives of Thio-carbonic Acid—Thiocyanogen and its Derivatives, Thiocyanic Acid and the Thiocyanates.

CHAPTER IV. Selenium 286

Occurrence, Extraction and Purification—The Allotropy of Selenium—Colloidal Selenium—General Physical Properties of Selenium—Chemical Properties—Applications of Element—Physiological Action—Atomic Weight—Valency—Constitution of Selenium Molecule—Detection and Estimation of Selenium.

CHAPTER V. Compounds of Selenium 311

GENERAL.

SELENIUM AND HYDROGEN :—Hydrogen Selenide and the Metallic Selenides.

COMPOUNDS OF SELENIUM WITH THE HALOGENS :—Fluorides, Chlorides, Bromides, Mixed Halides, Selenium and Iodine, Oxyfluoride, Oxychlorides, Oxybromide, Chloroselenic Acid.

SELENIUM AND OXYGEN :—General—Selenium Dioxide, Selenious Acid and the Selenites—Selenium Trioxide, Selenic Acid and the Selenates—Perseleic Acid.

COMPOUNDS CONTAINING SELENIUM AND SULPHUR :—Selenium Sulphoxide—Selenothionic Acids.

SELENIUM AND NITROGEN :—Selenium Nitride—Nitrosylselenic Acid.

SELENIUM AND PHOSPHORUS :—Phosphorus Subselelide, Phosphorus Monoselenide, Tetraphosphorus Triselenide, Phosphorus Triselenide, Phosphorus Pentaselenide—Phosphorus Chloroselenide—Selenophosphates and Oxy-selenophosphates.

SELENIUM AND CARBON :—Carbon Diselenide, Carbon Subselelides, Carbon Oxyselelide, Carbon Sulphidoselenide.

SELENIUM AND CYANOGEN :—Cyanogen Selenides—Selenocyanic Acid and the Selenocyanates.

SELENIUM AND SILICON :—Silicon Selenide.

SELENIUM AND BORON :—Selenium Boride.

CHAPTER VI. Tellurium 350

Occurrence, Early History, Extraction, Purification—Physical Properties—Chemical Properties—Physiological Action—Atomic Weight—Alloys—Detection and Estimation.

CHAPTER VII. Compounds of Tellurium 369

GENERAL.

TELLURIUM AND HYDROGEN :—Hydrogen Telluride.

TELLURIUM AND FLUORINE :—Tellurium Tetrafluoride, Tellurium Hexafluoride, Tellurium Oxyfluorides.

TELLURIUM AND CHLORINE :—Tellurium Dichloride, Tellurium Tetrachloride—Tellurium Perchlorate.

TELLURIUM AND BROMINE :—Tellurium Dibromide, Tellurium Tetrabromide, Tellurium Oxybromides.

CONTENTS.

xv
PAGE

TELLURIUM AND IODINE :—Tellurium Tetra-iodide.	
TELLURIUM AND OXYGEN :—Tellurium Monoxide—Tellurium Dioxide and the Tellurites—Tellurium Trioxide, Telluric Acids and the Tellurates.	
TELLURIUM AND SULPHUR :—Tellurium Disulphide, Tellurium Sulphoxide, Tellurium Sulphates, Telluropentathionic Acid.	
TELLURIUM AND SELENIUM :—Tellurium Selenate.	
TELLURIUM AND NITROGEN :—Tellurium Nitride, Tellurium Nitrite, Basic Tellurium Nitrate.	
TELLURIUM AND CARBON :—Carbon Sulphidotelluride.	
TELLURIUM AND CYANOGEN :—Tellurium Dicyanide.	

NAME INDEX	392
SUBJECT INDEX	414

LIST OF CHIEF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
<i>Afhandl. Fys. Kem.</i>	Afhandlingar i Fysik, Kemi och Mineralogi.
<i>Amer. Chem. J.</i>	American Chemical Journal.
<i>Amer. J. Sci.</i>	American Journal of Science.
<i>Anal. Fis. Quim.</i>	Anales de la Sociedad Española Física y Química.
<i>Analyst</i>	The Analyst.
<i>Annalen</i>	Justus Liebig's Annalen der Chemie.
<i>Ann. Chim.</i>	Annales de Chimie (1719-1815, and 1914+).
<i>Ann. Chim. anal.</i>	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie, et à la Biologie.
<i>Ann. Chim. Phys.</i>	Annales de Chimie et de Physique (Paris) (1816-1913).
<i>Ann. Mines</i>	Annales des Mines.
<i>Ann. Pharm.</i>	Annalen der Pharmacie (1832-1839).
<i>Ann. Phys. Chem.</i>	Annalen der Physik und Chemie (1819-1899).
<i>Ann. Physik</i>	Annalen der Physik (1799-1818, and 1900+).
<i>Ann. Physik, Beibl.</i>	Annalen der Physik, Beiblattes.
<i>Ann. Sci. Univ. Jassy</i>	Annales scientifiques de l'Université de Jassy.
<i>Arbeiten Kaiserl. Gesundheits- amte</i>	Arbeiten aus dem Kaiserlichen Gesundheitsamte.
<i>Arch. exp. Pathol. Pharmak.</i>	Archiv für experimentelle Pathologie und Pharmakologie.
<i>Arch. Pharm.</i>	Archiv der Pharmazie.
<i>Arch. Sci. phys. nat.</i>	Archives des Sciences physique et naturelles, Genève.
<i>Atti Acc. Torino</i>	Atti della Reale Accademia delle Scienze di Torino.
<i>Atti R. Accad. Lincei</i>	Atti della Reale Accademia Lincei.
<i>B.A. Reports</i>	British Association Reports.
<i>Ber.</i>	Berichte der Deutschen chemischen Gesellschaft.
<i>Ber. Akad. Ber.</i>	See <i>Sitzungsber. K. Akad. Wiss. Berlin</i> .
<i>Ber. Deut. pharm. Ges.</i>	Berichte der Deutschen pharmazeutischen Gesellschaft.
<i>Ber. Deut. physikal. Ges.</i>	Berichte der Deutschen physikalischen Gesellschaft.
<i>Bot. Zeit.</i>	Botanische Zeitung.
<i>Bul. Soc. Stiinte Cluj.</i>	Buletinul Societății de Științe din Cluj.
<i>Bull. Acad. roy. Belg.</i>	Académie royale de Belgique—Bulletin de la Classe des Sciences.
<i>Bull. Acad. Sci. Cracow</i>	Bulletin international de l'Académie des Sciences de Cracovie.
<i>Bull. de Belg.</i>	Bulletin de la Société chimique Belgique.
<i>Bull. Sci. Pharmacol.</i>	Bulletin des Sciences Pharmacologiques.
<i>Bull. Soc. chim.</i>	Bulletin de la Société chimique de France.
<i>Bull. Soc. franç. Min.</i>	Bulletin de la Société française de Minéralogie.
<i>Bull. Soc. min. de France</i>	Bulletin de la Société minéralogique de France.
<i>Bull. U.S. Geol. Survey</i>	Bulletins of the United States Geological Survey.
<i>Centr. Min.</i>	Centralblatt für Mineralogie.
<i>Chem. Ind.</i>	Die Chemische Industrie.
<i>Chem. News</i>	Chemical News.
<i>Chem. Weekblad</i>	Chemisch Weekblad.
<i>Chem. Zeit.</i>	Chemiker Zeitung (Cöthen).
<i>Chem. Zentr.</i>	Chemisches Zentralblatt.
<i>Compt. rend.</i>	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences (Paris).
<i>Croll's Annalen</i>	Chemische Annalen für die Freunde der Naturlehre, von L. Croll.
<i>Dingl. poly. J.</i>	Dingler's polytechnisches Journal.

ABBREVIATED TITLE.	JOURNAL.
<i>Drude's Annalen</i> . . .	<i>Annalen der Physik</i> (1900-1906).
<i>Electroch. Met. Ind.</i> . . .	Electrochemical and Metallurgical Industry.
<i>Eng. and Min. J.</i> . . .	Engineering and Mining Journal.
<i>Gazzetta</i> . . .	<i>Gazzetta chimica italiana</i> .
<i>Gehlen's Allg. J. Chem.</i> . . .	Allgemeines Journal der Chemie.
<i>Geol. Mag.</i> . . .	Geological Magazine.
<i>Gilbert's Annalen</i> . . .	<i>Annalen der Physik</i> (1799-1824).
<i>Giorn. di Scienze Naturali ed Econ.</i> . . .	<i>Giornale di Scienze Naturali ed Economiche</i> .
<i>Helv. Chim. Acta</i> . . .	<i>Helvetica Chim. Acta</i> .
<i>Int. Zeitsch. Metallographie</i> . . .	Internationale Zeitschrift für Metallographie.
<i>Jahrb. kk. geol. Reichsanst.</i> . . .	Jahrbuch der kaiserlich-königlichen geologischen Reichsanstalt.
<i>Jahrb. Miner.</i> . . .	Jahrbuch für Mineralogie.
<i>Jahresber.</i> . . .	Jahresbericht über die Fortschritte der Chemie.
<i>Jenaische Zeitsch.</i> . . .	Jenaische Zeitschrift für Naturwissenschaft.
<i>J. Amer. Chem. Soc.</i> . . .	Journal of the American Chemical Society.
<i>J. Chem. Soc.</i> . . .	Journal of the Chemical Society.
<i>J. Chim. phys.</i> . . .	Journal de Chimie physique.
<i>J. Gasbeleuchtung</i> . . .	Journal für Gasbeleuchtung.
<i>J. Geology</i> . . .	Journal of Geology.
<i>J. Ind. Eng. Chem.</i> . . .	Journal of Industrial and Engineering Chemistry.
<i>J. Inst. Metals</i> . . .	Journal of the Institute of Metals.
<i>J. Miner. Soc.</i> . . .	Mineralogical Magazine and Journal of the Mineralogical Society.
<i>J. Pharm. Chim.</i> . . .	Journal de Pharmacie et de Chimie.
<i>J. Physical Chem.</i> . . .	Journal of Physical Chemistry.
<i>J. Physique</i> . . .	Journal de Physique.
<i>J. prakt. Chem.</i> . . .	Journal für praktische Chemie.
<i>J. Russ. Phys. Chem. Soc.</i> . . .	Journal of the Physical and Chemical Society of Russia (Petrograd).
<i>J. Soc. Chem. Ind.</i> . . .	Journal of the Society of Chemical Industry.
<i>Landw. Jahrb.</i> . . .	Landwirtschaftliche Jahrbücher.
<i>Mem. Coll. Sci. Kyōtō</i> . . .	Memours of the College of Science, Kyōtō Imperial University.
<i>Mém. Paris Acad.</i> . . .	Mémoires présentés par divers savants à l'Académie de Sciences de l'Institut de France.
<i>Monatsh.</i> . . .	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
<i>Mon. scient.</i> . . .	Moniteur scientifique.
<i>Münch. Med. Wochenschr.</i> . . .	Münchener Medizinische Wochenschrift.
<i>Nature</i> . . .	Nature.
<i>Nuovo Cim.</i> . . .	Il nuovo Cimento.
<i>Oesterr. Chem. Zeit.</i> . . .	Oesterreichische Chemiker-Zeitung.
<i>Öfvers. K. Vet.-Akad. Förh.</i> . . .	Öfversigt af Kongliga Vetenskaps-Akademiens Förhandlingar.
<i>Pflüger's Archiv</i> . . .	Archiv für die gesammte Physiologie des Menschen und der Thiere.
<i>Pharm. Post</i> . . .	Pharmazeutische Post.
<i>Pharm. Zentr.-h.</i> . . .	Pharmazeutische Zentrallhalle.
<i>Phil. Mag.</i> . . .	Philosophical Magazine (The London, Edinburgh, and Dublin).
<i>Phil. Trans.</i> . . .	Philosophical Transactions of the Royal Society of London.
<i>Phys. Review</i> . . .	Physical Review.
<i>Physikal. Zeitsch.</i> . . .	Physikalische Zeitschrift.
<i>Pogg. Annalen</i> . . .	Poggendorff's Annalen der Physik und Chemie (1824-1877).
<i>Proc. Chem. Soc.</i> . . .	Proceedings of the Chemical Society.
<i>Proc. K. Akad. Wetensch. Amsterdam</i> . . .	Koninklijke Akademie van Wetenschappen te Amsterdam Proceedings (English Version).
<i>Proc. Roy. Irish Acad.</i> . . .	Proceedings of the Royal Irish Academy.
<i>Proc. Roy. Phil. Soc. Glasgow</i> . . .	Proceedings of the Royal Philosophical Society of Glasgow.
<i>Proc. Roy. Soc.</i> . . .	Proceedings of the Royal Society of London.
<i>Proc. Roy. Soc. Edin.</i> . . .	Proceedings of the Royal Society of Edinburgh.

LIST OF CHIEF ABBREVIATIONS.

rix

ABBREVIATED TITLE.	JOURNAL.
<i>Rec. Trav. chim.</i> . . .	Recueil des Travaux chimiques des Pays-Bas et de la Belgique.
<i>Roy. Inst. Reports</i> . . .	Reports of the Royal Institution.
<i>Schweigger's J.</i> . . .	Journal für Chemie und Physik.
<i>Sci. Proc. Roy. Dubl. Soc.</i> . . .	Scientific Proceedings of the Royal Dublin Society.
<i>Sitzungsber. K. Akad. Wiss. Berlin.</i> . . .	Sitzungsberichte der Königlich-Preussischen Akademie der Wissenschaften zu Berlin.
<i>Sitzungsber. K. Akad. Wiss. Wien</i> . . .	Sitzungsberichte der Königlich-Bayerischen Akademie der Wissenschaften zu Wien.
<i>Techn. Jahresber.</i> . . .	Jahresbericht über die Leistungen der Chemischen Technologie.
<i>Trans. Amer. Electrochem. Soc.</i> . . .	Transactions of the American Electrochemical Society.
<i>Trans. Chem. Soc.</i> . . .	Transactions of the Chemical Society.
<i>Trans. Inst. Min. Eng.</i> . . .	Transactions of the Institution of Mining Engineers.
<i>Trav. et Mém. du Bureau intern. des Poids et Mes.</i> . . .	Travaux et Mémoires du Bureau International des Poids et Mesures.
<i>Verh. Ges. deut. Naturforsch. Aerzte</i> . . .	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
<i>Wied. Annalen</i> . . .	Wiedemann's Annalen der Physik und Chemie (1877-1899).
<i>Wissenschaftl. Abhandl. phys.-tech. Reichsanst.</i> . . .	Wissenschaftliche Abhandlungen der physikalisch-technischen Reichsanstalt.
<i>Zeitsch. anal. Chem.</i> . . .	Zeitschrift für analytische Chemie.
<i>Zeitsch. angew. Chem.</i> . . .	Zeitschrift für angewandte Chemie.
<i>Zeitsch. anorg. Chem.</i> . . .	Zeitschrift für anorganische Chemie.
<i>Zeitsch. Chem.</i> . . .	Kritische Zeitschrift für Chemie.
<i>Zeitsch. Chem. Ind. Kolloide</i> . . .	Zeitschrift für Chemie und Industrie des Kolloide (continued as Kolloid-Zeitschrift).
<i>Zeitsch. Elektrochem.</i> . . .	Zeitschrift für Elektrochemie.
<i>Zeitsch. Kryst. Min.</i> . . .	Zeitschrift für Kristallographie und Mineralogie.
<i>Zeitsch. Nahr. Genuss-m.</i> . . .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
<i>Zeitsch. physikal. Chem.</i> . . .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
<i>Zeitsch. physiol. Chem.</i> . . .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
<i>Zeitsch. wiss. Photochem.</i> . . .	Zeitschrift für wissenschaftliche Photographie, Photo-physik, und Photochemie.

TABLE OF DATES OF ISSUE OF JOURNALS.

For the sake of easy reference, a list is appended of the more important journals in chronological order, giving the dates of issue of their corresponding series and volumes. In certain cases the volumes have appeared with considerable irregularity; in others it has occasionally happened that volumes begun in one calendar year have extended into the next year, even when this has not been the general habit of the series. To complicate matters still further, the title-pages in some of these latter volumes bear the later date—a most illogical procedure. In such cases the volume number appears in the accompanying columns opposite both years. In a short summary of this kind it is impossible to give full details in each case, but the foregoing remarks will serve to explain several apparent anomalies.

Year.	Amer J Sci	Ann Chim. Phys	Ann. Min.	Arch Pharm.	Dugl. Poly. J.	Gilbert's Annalen.	J Pharm. Chim.	Phil. Mag.	Phil. Trans.	Pogg Annalen.
1800	..	(1) 32-35	4-6	...	5-8	90	...
1	.	36-39	7-9	...	8-11	91	...
2	...	40-43	10-12	...	11-14	92	...
3	...	44-47	13-15	...	14-17	93	...
4	...	48-51	16-18	...	17-20	94	...
1805	.	52-55	19-21	...	20-23	95	...
6	.	56-60	22-24	...	23-26	96	...
7	...	61-64	25-27	...	26-29	97	...
8	...	65-68	28-30	...	29-32	98	...
9	...	69-72	31-33	(1) 1*	33, 34	99	...
1810	...	73-76	34-36	2	35, 36	100	...
11	...	77-80	37-39	3	37, 38	101	...
12	...	81-84	40-42	4	39, 40	102	...
13	...	85-88	43-45	5	41, 42	103	...
14	...	89-92	46-48	6	43, 44	104	...
1815	...	93-96	49-51	(2) 1	45, 46	105	...
16	...	(2) 1-3	52-54	2	47, 48	106	...
17	...	4-6	1, 2	55-57	3	49, 50	107	...
18	...	7-9	3	58-60	4	51, 52	108	...
19	(1) 1	10-12	4	61-63	5	53, 54	109	...
1820	2	13-15	5	...	1-3	64-66	6	55, 56	110	...
21	3	16-18	6	...	4-6	67-69	7	57, 58	111	...
22	4, 5	19-21	7	1, 2	7-9	70-72	8	59, 60	112	...
23	6	22-24	8	3-6	10-12	73-75	9	61, 62	113	...
24	7, 8	25-27	9	7-10	13-15	76	10	63, 64	114	1, 2
1825	9	28-30	10, 11	11-14	16-18	19-22	11	65, 66	115	3-5
26	10, 11	31-33	12, 13	15-19	19-22	23-26	12	67, 68	116	6-8
27	12	34-36	(2) 1, 2	20-23	23-26	27-30	13	(2) 1, 2	117	9-11
28	13, 14	37-39	3, 4	24-26	27-30	31-34	14	3, 4	118	12-14
29	15, 16	40-42	5, 6	27-30	31-34	Continued as Pogg. Annalen.	15	5, 6	119	15-17

* First series known as *Bulletin de Pharmacie*.

Year.	Amer. J. Sci.	Annalen.	Ann. Chim. Phys.	Ann. Minera.	Arch. Pharm.	Bull. Soc. chim.	Compt. rend.	Dingl. poly. J.	J. Pharm. Chim.	J. prakt. Chem.	Mon. scient.	Phil. Mag.	Phil. Trans.	Pogg. Annalen.	Proc. Roy. Soc.	Quart. J. Chem. Soc.	Sitzungsber. K. Akad. Wiss. Wien.
1880	17, 18	...	43-46	7-8	31-34	35-38	16	7, 8	120	18-20
81	19, 20	...	46-48	...	36-39	39-42	17	9, 10	121	21-23
82	21, 22	1-4	49-51	(3) 1, 2	40-43	43-47	18	11 (3) 1	122	24-26	1
83	23, 24	5-8	52-55	3, 4	44-47	48-50	19	2, 3	123	27-30	2
84	25-27	9-12	56-57	5, 6	48-50	51-54	20	1-3	...	4, 5	124	31-33
1885	28, 29	18-16	58-60	7, 8	(2) 1-4	...	1	55-58	21	4-6	...	6, 7	125	34-36
86	30, 31	17-20	61-63	9, 10	6-8	...	2, 3	59-62	22	7-9	...	8, 9	126	37-39
87	32, 33	21-24	64-66	11, 12	9-12	...	4, 5	63-66	23	10-12	...	10, 11	127	40-42	8
88	34, 35	25-28	67-69	13, 14	13-16	...	6, 7	67-70	24	13-15	...	12, 13	128	43-45
89	36, 37	29-32	70-72	15, 16	17-20	...	8, 9	71-74	25	16-18	...	14, 15	129	46-48
1890	38, 39	33-36	73-75	17, 18	21-24	...	10, 11	75-78	26	19-21	...	16, 17	130	49-51
41	40, 41	37-40	(8) 1-3	19, 20	25-28	...	12, 13	79-82	27	22-24	...	18, 19	131	52-54
42	42, 43	41-44	4-6	(4) 1, 2	29-32	...	14, 15	83-86	(3) 1, 2	25-27	...	20, 21	132	55-57
43	44, 45	45-48	7-9	3, 4	33-36	...	16, 17	87-90	3, 4	28-30	...	22, 23	133	58-60	4
44	46, 47	49-52	10-12	5, 6	37-40	...	18, 19	91-94	5, 6	31-33	...	24, 25	134	61-63
1895	48-50	53-56	13-15	7, 8	41-44	...	20, 21	95-98	7, 8	34-36	...	26, 27	135	64-66
46	(2) 1, 2	57-60	16-18	9, 10	45-48	...	22, 23	99-102	9, 10	37-39	...	28, 29	136	67-69
47	3, 4	61-64	19-21	11, 12	49-52	...	24, 25	103-106	11, 12	40-42	...	30, 31	137	70-72	...	1	...
48	5, 6	65-68	22-24	13, 14	53-56	...	26, 27	107-110	13, 14	43-45	...	32, 33	138	73-75	...	1, 2	...
49	7, 8	69-72	25-27	15, 16	57-60	...	28, 29	111-114	15, 16	46-48	...	34, 35	139	76-78	...	2, 3	...
1890	9, 10	73-76	28-30	17, 18	61-64	...	30, 31	115-118	17, 18	49-51	...	36, 37	140	79-81	...	3	4, 5
51	11, 12	77-80	31-33	19, 20	65-68	...	32, 33	119-122	19, 20	52-54	...	(4) 1, 2	141	82-84	...	4	6, 7
52	13, 14	81-84	34-36	(5) 1, 2	69-72	...	34, 35	123-126	21, 22	55-57	...	3, 4	142	85-87	...	5	8, 9
53	15, 16	85-88	37-39	3, 4	73-76	...	36, 37	127-130	23, 24	58-60	...	5, 6	143	88-90	...	6	10, 11
54	17, 18	89-92	40-42	5, 6	77-80	...	38, 39	131-134	25, 26	61-63	...	7, 8	144	91-93	...	7	12-14
1895	19, 20	93-96	43-45	7, 8	81-84	...	40, 41	135-138	27, 28	64-66	...	9, 10	145	94-96	7	8	15-18
56	21, 22	97-100	46-48	9, 10	85-88	...	42, 43	139-142	29, 30	67-69	...	11, 12	146	97-99	8	9	19-23
57	23, 24	101-104	49-51	11, 12	89-92	...	44, 45	143-146	31, 32	70-72	(1) 1	13, 14	147	100-102	9	10	23-27
58	25, 26	105-108	52-54	13, 14	93-96	1	46, 47	147-150	33, 34	73-75	2	15, 16	148	103-105	...	11	28-33
59	27, 28	109-112	55-57	15, 16	97-100	1	48, 49	151-154	35, 36	76-78	3	17, 18	149	106-108	9, 10	12	34-38

* Often referred to by Series : Series 3, vols. 1-16, 1871-1886 ; Series 4, vols. 1-24, 1887-1910 ; Series 5, vols. 1-9, 1911-1919 (one vol. yearly).

TABLE OF DATES OF ISSUE OF JOURNALS.

xiii

Year.	Amer. Chem. J.	Amer. J. Sci.	Analyst.	Annalen.	Annalen Suppl.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm.	Ber.	Bull. Soc. chim.	Chem. News.	Chem. Trade J.	Chem. Zeit.
1860	...	29, 30	...	118-116	...	58-60	17, 18	101-104	...	2	1, 2
61	...	31, 32	...	117-120	1	61-63	19, 20	105-108	...	3	3, 4
62	...	33, 34	...	121-124	2	64-66	(6) 1, 2	109-112	...	4	5, 6
63	...	35, 36	...	125-128	2	67-69	3, 4	113-116	...	5	7, 8
64	...	37, 38	...	129-132	3	(4) 1-3	5, 6	117-120	...	(2) 1, 2	9, 10
1865	...	39, 40	...	133-136	3, 4	4-6	7, 8	121-124	...	3, 4	11, 12
66	...	41, 42	...	137-140	4	7-9	9, 10	125-128	...	5, 6	13, 14
67	...	43, 44	...	141-144	5	10-12	11, 12	129-132	...	7, 8	15, 16
68	...	45, 46	...	145-148	6	13-15	13, 14	133-136	1	9, 10	17, 18
69	...	47, 48	...	149-152	.	16-18	15, 16	137-140	2	11, 12	19, 20
1870	...	49, 50	...	153-156	7	19-21	17, 18	141-144	3	13, 14	21, 22
71	...	(3) 1, 2	...	157-160	.	22-24	19, 20	145-148	4	15, 16	23, 24
72	...	3, 4	...	161-164	8	25-27	(7) 1, 2	149-150, 201*	5	17, 18	25, 26
73	...	5, 6	...	165-170	...	28-30	3, 4	201-203	6	19, 20	27, 28
74	...	7, 8	...	171-174	.	(5) 1-3	5, 6	204, 205	7	21, 22	29, 30
1875	...	9, 10	...	175-179	.	4-6	7, 8	206, 207	8	23, 24	31, 32
76	...	11, 12	1	180-183	...	7-9	9, 10	208, 209	9	25, 26	33, 34
77	...	13, 14	2	184-189	...	10-12	11, 12	210, 211	10	27, 28	35, 36	...	1
78	...	15, 16	3	190-194	...	13-15	13, 14	212, 213	11	29, 30	37, 38	...	2
79	1	17, 18	4	195-199	...	16-18	15, 16	214, 215	12	31, 32	39, 40	...	8
1880	1, 2	19, 20	5	200-205	...	19-21	17, 18	216, 217	13	33, 34	41, 42	...	4
81	2, 3	21, 22	6	206-210	...	22-24	19, 20	218, 219	14	35, 36	43, 44	...	5
82	3, 4	23, 24	7	211-215	...	25-27	(8) 1, 2	220	15	37, 38	45, 46	...	6
83	4, 5	25, 26	8	216-221	...	28-30	3, 4	221	16	39, 40	47, 48	...	7
84	5, 6	27, 28	9	222-226	...	(6) 1-3	5, 6	222	17	41, 42	49, 50	...	8
1885	6, 7	29, 30	10	227-231	...	4-6	7, 8	223	18	43, 44	51, 52	...	9
86	7, 8	31, 32	11	232-236	...	7-9	9, 10	224	19	45, 46	53, 54	...	10
87	9	33, 34	12	237-242	...	10-12	11, 12	225	20	47, 48	55, 56	...	11
88	10	35, 36	13	243-249	...	13-15	13, 14	226	21	49, 50	57, 58	2, 8	12
89	11	37, 38	14	250-255	.	16-18	15, 16	227	22	(3) 1, 2	59, 60	4, 5	13

* Joining Series 1 and 2 together. Also written as (3) 1, 2, 3, etc.

Year.	Amer. Chem. J.	Amer. J. Sci.	Analyst.	Annalen.	Ann. Chim. Phys.	Ann. Mines.	Arch. Pharm.	Ber.	Bull. Soc. chim.	Chem. News.	Chem. Trade J.	Chem. Weekblad.	Chem. Zeit.	Compt. rend.
1890	12	39, 40	15	256-260	19-21	17, 18	228	23	3, 4	61, 62	6, 7	...	14	110, 111
91	13	41, 42	16	261-266	22-24	19, 20	229	24	5, 6	63, 64	8, 9	...	15	112, 113
92	14	43, 44	17	267-271	25-27	(9) 1, 2	230	25	7, 8	65, 66	10, 11	...	16	114, 115
93	15	45, 46	18	272-277	28-30	3, 4	231	26	9, 10	67, 68	12, 13	...	17	116, 117
94	16	47, 48	19	278-283	(7) 1-3	5, 6	232	27	11, 12	69, 70	14, 15	...	18	118, 119
1895	17	49, 50	20	284-288	4-6	7, 8	233	28	13, 14	71, 72	16, 17	...	19	120, 121
96	18	(4) 1, 2	21	289-293	7-9	9, 10	234	29	15, 16	73, 74	18, 19	...	20	122, 123
97	19	3, 4	22	294-298	10-12	11, 12	235	30	17, 18	75, 76	20, 21	...	21	124, 125
98	20	5, 6	23	299-303	13-15	13, 14	236	31	19, 20	77, 78	22, 23	...	22	126, 127
99	21, 22	7, 8	24	304-309	16-18	15, 16	237	32	21, 22	79, 80	24, 25	...	23	128, 129
1900	23, 24	9, 10	25	310-313	19-21	17, 18	238	33	23, 24	81, 82	26, 27	...	24	130, 131
1	25, 26	11, 12	26	314-319	22-24	19, 20	239	34	25, 26	83, 84	28, 29	...	25	132, 133
2	27, 28	13, 14	27	320-325	25-27	(10) 1, 2	240	35	27, 28	85, 86	30, 31	...	26	134, 135
3	29, 30	15, 16	28	326-329	28-30	3, 4	241	36	29, 30	87, 88	32, 33	...	27	136, 137
4	31, 32	17, 18	29	330-337	(8) 1-3	5, 6	242	37	31, 32	89, 90	34, 35	...	28	138, 139
1905	33, 34	19, 20	30	338-343	4-6	7, 8	243	38	33, 34	91, 92	36, 37	...	29	140, 141
6	35, 36	21, 22	31	344-350	7-9	9, 10	244	39	35, 36	93, 94	38, 39	...	30	142, 143
7	37, 38	23, 24	32	351-357	10-12	11, 12	245	40	(4) 1, 2	95, 96	40, 41	...	31	144, 145
8	39, 40	25, 26	33	358-363	13-15	13, 14	246	41	3, 4	97, 98	42, 43	...	32	146, 147
9	41, 42	27, 28	34	364-371	16-18	15, 16	247	42	5, 6	99, 100	44, 45	...	33	148, 149
1910	43, 44	29, 30	35	372-377	19-21	17, 18	248	43	7, 8	101, 102	46, 47	...	34	150, 151
11	45, 46	31, 32	36	378-385	22-24	19, 20	249	44	9, 10	103, 104	48, 49	...	35	152, 153
12	47, 48	33, 34	37	386-394	25-27	(11) 1, 2	250	45	11, 12	105, 106	50, 51	...	36	154, 155
13	49, 50	35, 36	38	395-401	28-30	3, 4	251	46	13, 14	107, 108	52, 53	...	37	156, 157
14	Publ. tion	37, 38	39	5, 6	252	47	15, 16	109, 110	54, 55	...	38	158, 159
1915	ceased	39, 40	40	253	48	17, 18	111, 112	56, 57	...	39	160, 161
16	...	41, 42	41	254	49	19, 20	113, 114	58, 59	...	40	162, 163
17	...	43, 44	42	255	50	21, 22	115, 116	60, 61	...	41	164, 165
18	...	45, 46	43	51	23, 24	117	62, 63	...	42	166, 167
19	...	47, 48	44	52	25, 26	118, 119	64, 65	...	43	168, 169

TABLE OF DATES OF ISSUE OF JOURNALS.

xxvii

Year.	Dingl. poly J.	Gazette.	J. Amer. Chem. Soc.	J. Chem. Soc.	J. Ind. Eng. Chem.	J. Pharm. Chim.	J. Physical Chem.	J. prakt. Chem.	J. Russ. Phys. Chem. Soc	J. Soc. Chem. Ind.	Monstsh.	Mon. * scient.	Nature.	Phil. Mag.
1890	275-278 279-282 283-286 287-290 291-294	20 21 22 23 24	12 13 14 15 16	57, 58 59, 60 61, 62 63, 64 65, 66	...	21, 22 23, 24 25, 26 27, 28 29, 30	...	41, 42 43, 44 45, 46 47, 48 49, 50	22 23 24 25 26	9	11 12 13 14 15	35, 36 37, 38 39, 40 41, 42 43, 44	41, 42, 43 43, 44, 45 45, 46, 47 47, 48, 49 49, 50, 51	29, 30 31, 32 33, 34 35, 36 37, 38
1895	295-298 299-302 303-306 307-310 311-314	25 26 27 28 29	17 18 19 20 21	67, 68 69, 70 71, 72 73, 74 75, 76	...	(6) 1, 2 3, 4 5, 6 7, 8 9, 10	...	51, 52 53, 54 55, 56 57, 58 59, 60	27 28 29 30 31	14	16 17 18 19 20	45, 46 47, 48 49, 50 51, 52 53, 54	51, 52, 53 53, 54, 55 55, 56, 57 57, 58, 59 59, 60, 61	39, 40 41, 42 43, 44 45, 46 47, 48
1900	315 316 317 318 319	30 31 32 33 34	22 23 24 25 26	77, 78 79, 80 81, 82 83, 84 85, 86	...	11, 12 13, 14 15, 16 17, 18 19, 20	4 5 6 7 8	61, 62 63, 64 65, 66 67, 68 69, 70	32 33 34 35 36	19	21 22 23 24 25	55, 56 57 58 59 60, 61	61, 62, 63 63, 64, 65 65, 66, 67 67, 68, 69 69, 70, 71	49, 50 (6) 1, 2 3, 4 5, 6 7, 8
1905	320 321 322 323 324	35 36 37 38 39	27 28 29 30 31	87, 88 89, 90 91, 92 93, 94 95, 96	...	21, 22 23, 24 25, 26 27, 28 29, 30	9 10 11 12 13	71, 72 73, 74 75, 76 77, 78 79, 80	37 38 39 40 41	24	26 27 28 29 30	62, 63 64, 65 66, 67 68, 69 70, 71	71, 72, 73 73, 74, 75 75, 76, 77 77, 78, 79 79-82	9, 10 11, 12 13, 14 15, 16 17, 18
1910	325 326 327 328 329	40 41 42 43 44	32 33 34 35 36	97, 98 99, 100 101, 102 103, 104 105, 106	2 3 4 5 6	(7) 1, 2 3, 4 5, 6 7, 8 9, 10	14 15 16 17 18	81, 82 83, 84 85, 86 87, 88 89, 90	42 43 44 45 46	29	31 32 33 34 35	72, 73 74, 75 76, 77 78, 79 80, 81	82-85 85-88 88, 89, 90 90, 91, 92 92, 93, 94	19, 20 21, 22 23, 24 25, 26 27, 28
1915	...	45	37	107, 108	7	11, 12	19	91, 92	47	34	36	82	94, 95, 96	29, 30
1916	...	46	38	109, 110	8	13, 14	20	93, 94	48	35	37	83	96, 97, 98	31, 32
1917	...	47	39	111, 112	9	15, 16	21	95, 96	...	36	38	84	98, 99, 100	33, 34
1918	...	48	40	113, 114	10	17, 18	22	97, 98	...	37	39	85	100-102	35, 36
1919	...	49	41	115, 116	11	19, 20	23	99, 100	...	38	40	86	102-104	37, 38

* See footnote, p. xxii.

Year.	Phil. Trans.	Physikal. Zeitsch.	Proc. Chem. Soc.	Proc. Roy. Soc.	Rec. Trav. Chim.	Sitzungsber. K. Akad. Wiss. Wien.	Stahl und Eisen.	Wied. Annalen.	Zeitsch. anal. Chem.	Zeitsch. angew. Chem.	Zeitsch. Elektrochem.	Zeitsch. Kryst. Min.	Zeitsch. physikal. Chem.
1890	A. 181	...	6	47, 48, 49	9	99	10	39-41	29	3	...	16, 17, 18	5, 6
91	182	...	7	49, 50	10	100	11	42-44	30	4	...	19, 20	7, 8
92	183	...	8	50, 51, 52	11	101	12	45-47	31	5	...	20, 21	9, 10
93	184	...	9	52, 53, 54	12	102	13	48-50	32	6	...	21, 22	11, 12
94	185	...	10	55, 56, 57	13	103	14	51-53	33	7	1	23, 24	13-15
1895	186	...	11	57, 58, 59	14	104	15	54-56	34	8	1, 2	24, 25	16-18
96	187, 188	...	12	59, 60	15	105	16	57-59	35	9	11, 12, 13	26-28	19-21
97	189, 190	...	13	60, 61, 62	16	106	17	60-63	36	10	3, 4	28, 29	22-24
98	191	...	14	62, 63, 64	17	107	18	64-66	37	11	4, 5	29-31	25-27
99	192, 193	...	15	64, 65, 66	18	108	19	67-69	38	12	5, 6	31, 32	28-31
1900	194, 195	1	16	66, 67	19	109	20	Con-	39	13	6, 7	32-34	32-35
1	196, 197	2	17	68, 69	20	110	21	tinued as	40	14	7	34-36	36-38
2	198, 199	3	18	69, 70	21	111	22	Annalen	41	15	8	36, 37	39-42
3	200-202	4	19	71, 72	22	112	23	der	42	16	9	37-39	43-46
4	203	5	20	72, 73, 74	23	113	24	Physik.	43	17	10	39, 40	47-49
1905	204, 205	6	21	74-76	24	114	25		44	18	11	40-42	50-53
6	206	7	22	A. 77, 78	25	115	26		45	19	12	42, 43	54-57
7	207	8	23	78, 79, 80	26	116	27		46	20	13	43, 44	58-60
8	207-209	9	24	80, 81	27	117	28		47	21	14	44-46	61-64
9	209, 210	10	25	82, 83	28	118	29		48	22	15	46, 47	65-69
1910	210	11	26	83, 84	29	119	30		49	23	16	48, 49	70-74
11	210, 211	12	27	84, 85, 86	30	120	31		50	24	17	49, 50	75-77
12	211, 212	13	28	86, 87	31	121	32		51	25	18	50-52	78-80
13	212, 213	14	29	88, 89	32	122	33		52	26	19	52, 53	81-86
14	213, 214	15	30	89, 90	33	123	34		53	27	20	54	86-88
1915	215, 216	16	Publication	...	34	...	35		54	28	21	55	89, 90
16	216, 217	17	of matter	...	35	...	36		55	29	22	...	91, 92
17	217	18	of scientific	...	36, 37	...	37		56	30	23	...	92
18	217	...	interest now	...	37	...	38		57	31	24	No	92
19	abandoned.	...	38	...	39		58	32	25	issue*	...

* Remainder of vol. 55 appeared in 1920.

proceeded
its action
taminat
in son
positi

fre
fo

A TEXT-BOOK OF
INORGANIC CHEMISTRY.
VOLUME VII. PART II.

SULPHUR.

9

proceeded further, sulphuric acid would have been produced, which by its action on the calcareous rocks would account for the frequent contamination of the sulphur with sulphates. It is possible, however, that in some cases the deposits of sulphur owe their existence to the decomposition of pre-existing mineral sulphates.¹

Hydrogen sulphide is present in many mineral springs, and even free sulphur is occasionally found therein.² Many metallic sulphides, for example, *iron pyrites, galena, zinc blende, stibnite* and *cinnabar*, occur abundantly. Sulphur dioxide, sulphites, sulphuric acid and sulphates are also found in nature, more especially in waters springing from volcanic earth, whilst the sulphates of certain metals such as calcium, barium and magnesium exist in large deposits.

In the organic world sulphur is sometimes found free; certain micro-organisms and algæ which thrive in water containing hydrogen sulphide enclose sulphur in a non-crystalline condition.³ Combined sulphur is present in albuminoid substances, and is therefore found in all living animal⁴ and vegetable matter. The presence of sulphur in coal in various forms⁵ is well known. Certain essential oils such as those derived from mustard and garlic contain combined sulphur, as also do petroleum and asphaltum in small and variable quantity.

Extraction.—Of the total annual output of nearly 2½ million tons of sulphur, almost the whole is produced by the United States and Sicily. The production figures for 1928 were as follows: ⁶

United States	1,981,873 tons.
Italy (including Sicily)	322,481 „
Spain, sulphur rock	74,632 „
„ , refined sulphur	19,491 „
Japan, sulphur rock	13,109 „
„ , refined sulphur	68,962 „
United Kingdom and Irish Free State, spent oxide (average sulphur content 48·8 per cent.)	174,000 „

The remarkable rise in recent years of the industry in the United States is largely due to the introduction of new methods in mining the subterranean deposits. In Sicily and Italy, where the extraction is an old industry, the “ore” rarely contains much above 40 per cent. of sulphur and is considered rich if above 30 per cent. The process of extraction is based on the liquation of the element. Although attempts have been made to supply the necessary heat, directly or indirectly, by means of ordinary fuels, no system has proved so cheap as that utilising

¹ Kraus and Hunt, *Amer. J. Sci.*, 1906, [iv.], 21, 237; Kruegger and Ewald, *Centr. Min.*, 1912, 638. For a method of formation by the decomposition of previously-formed sulphites, see Bayer & Co., *German Patent*, 265167 (1913). For the probable origin of deposits of sulphur at Monte Solfonoso, Italy, see Onorato, *Atti R. Accad. Lincei*, 1928, [vi.], 8, 243.

² Moissan, *Compt. rend.*, 1902, 135, 1278.

³ Etard and Olivier, *Compt. rend.*, 1882, 95, 846; Olivier, *ibid.*, 1888, 106, 1806; Kramer and Spilker, *Ber.*, 1899, 32, 2941.

⁴ See Wohlgemuth, *Zeitsch. physiol. Chem.*, 1905, 43, 469; also Timár, *Biochem. Zeitsch.*, 1928, 202, 365.

⁵ For a recent investigation into the nature of the sulphur in Canadian coal and coke, see Nicolls, *Canada Dept. Mines Fuel Invest.*, 1926, 34.

⁶ Imperial Institute, *The Mineral Industry, Statistical Summary*, 1929-30.

the heat of combustion of a part of the sulphur itself. The old *calcarone method*, which is now rapidly becoming obsolete, consisted in building up, usually against the side of a hill and on a sloping floor, a large heap (calcarone) of sulphur ore in such a manner as to give a mass containing vertical air channels; the outside of the heap was protected by a coating of earth or other mineral substance. The mass was then fired near the base, and by carefully regulating the course of the combustion, which lasted for several weeks, the proportion of sulphur lost by atmospheric oxidation (and by the reduction of calcium sulphate to sulphide) could be limited to approximately one-third, the remainder collecting on the floor, whence it was periodically run off into rectangular moulds. The product thus obtained contained 85 to 90 per cent. of sulphur.

The foregoing process, besides being uneconomical, suffered great disadvantage owing to the liberation of immense volumes of sulphur dioxide into the atmosphere. This evil is mitigated to a considerable extent in the more modern process. The sulphur ore is placed in a group or cycle of small kilns (*fornelli*), built of brickwork and so arranged that the hot gases generated in the first kiln pass successively through the remainder of the kilns, the full number of kilns frequently being six. In some cases the kiln is in the form of an oven covered by a cupola, inside which is a smaller cupola containing a coke fire. By the time fusion is complete in the first oven, the contents of the second are already heated to burning temperature, so that the heat of combustion of the sulphur is more completely utilised and a smaller proportion of sulphur dioxide produced.¹ The pollution of the atmosphere relative to the output of sulphur is thus diminished; a further diminution in the deleterious influence of the sulphur dioxide on vegetation can be effected by restricting the process to certain periods of the year, although with the newest types of plant this is not necessary. The yield of sulphur obtained by these later methods is much larger (sometimes by 50 per cent.) than by the calcarone method, and the working is much more rapid, the reaction in the kilns generally being complete after a few days.

The most important deposits of sulphur in the world are those of Louisiana and Texas, U.S.A., where *H. Frasch's method of extraction* is followed.² This obviates the formation of sulphur dioxide and at the same time yields a product of such a degree of purity (in some wells as high as 99.9 per cent.) as to be suitable in most cases for direct use. A boring is made in the earth down to the sulphur stratum so that a continuous pipe can pass thence to the surface; the pipe consists of three concentric tubes (see fig. 1). Superheated water, e.g. at 150° C., is forced down the annular spaces A, A, between the outer tubes, in order to melt the sulphur in the neighbourhood of the end of the boring. A blast of heated air down the inmost tube, B, then causes the molten sulphur to be carried up between the two inner tubes to the surface, where it is collected.³

Smaller quantities of sulphur are obtained in the preliminary roasting of certain sulphide ores where the desulphurised mass is required for

¹ For a description of a new type of externally heated furnace, see Ricevuto and Buogo, *Atti II Cong. Naz. Chim. pura appl.*, 1926, 757; *Chem. Zentr.*, 1928, ii., 379.

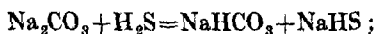
² Frasch, *Zeitsch. angew. Chem.*, 1905, 18, 1009; 1906, 19, 926. See also *The Chemical Age*, October 1921, 517.

³ See also Lundy and Burns, *American Patent*, 1612453 (1926). A mixture of hot water and finely divided earthy material is injected into the sulphur-bearing formation.

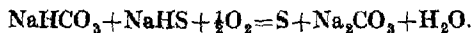
further operations. Iron pyrites itself is sometimes treated in this way, the residual ferrous sulphide being applied to purposes such as the manufacture of sulphuric acid.

The iron oxide used in the purification of coal gas gradually becomes richer in sulphur and can repeatedly be revived by exposure to air until the sulphur amounts to about 40 per cent. of the whole; the mixture is then of greater value as a source of sulphur. The "spent oxide," as it is commonly termed, is frequently applied to the production of sulphur dioxide or sulphuric acid, but the extraction of its sulphur by carbon disulphide has been effected as a successful commercial process; using the system of "counter-currents" the mass is exhausted of sulphur, whilst a saturated solution of sulphur is obtained, from which the solvent can be distilled and returned to the extraction process.

In many coal- and oil-gas works in the Western States of America the Koppers process for the removal of hydrogen sulphide from the gas is employed. This consists of passing the gas up towers filled with wooden hurdles over which a dilute sodium carbonate solution is sprayed. The following reaction occurs:



the sulphur is then recovered from the solution by agitation in intimate contact with air in an emulsifying machine, a catalyst also being present:



The catalyst used is colloidal nickel sulphide. The sulphur is run off from the surface, and after filtering and washing is obtained as a paste containing 55 per cent. of water. After drying, a product is obtained which is more toxic than most other forms of sulphur and is very effective in agricultural work as a fungicide; the particles are almost of colloidal size, most being less than $15\ \mu$.¹

A further method of obtaining sulphur from sulphide ores consists in heating the latter under high vacuum; the sulphur vaporises and is condensed in a suitable receiver.²

Sulphur is also obtained from alkali waste (p. 56).

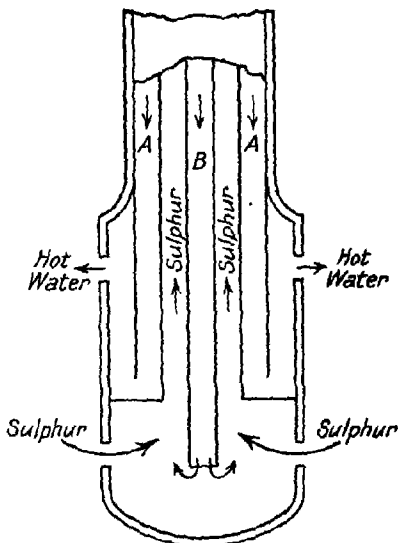


FIG. 1.—Lower End of Pipe Used in Frasch Process.

¹ Candall, *Chem. Met. Eng.*, 1927, 34, 143; 1928, 35, 407.

² Wilkinson, *American Patent*, 1560928 (1925); *Marx, American Patents*, 1574988-9 (1928).

Refining.—The crude Sicilian sulphur, partly on account of the lack of fuel, is exported to be refined elsewhere. In the subsequent commercial purification the processes involved are decantation and sublimation or distillation. After melting in cylindrical vessels and allowing the mechanical impurities to settle, the sulphur is run into horizontal iron retorts which open into a large vaulted chamber. If distillation occurs slowly, the temperature of the receiving chamber will not attain the melting-point of sulphur and the vapour issuing from the retorts will condense directly to a solid powder, which constitutes "*flowers of sulphur*" or "*sublimed sulphur*." Rapid distillation will cause the temperature of the receiver to rise above the melting-point of sulphur and the vapour will then condense as a liquid, which is periodically tapped off into wet wooden moulds of rectangular or cylindrical shape, the resulting product being known as "*roll sulphur*." Moulds constructed of aluminium or its alloys have also been found suitable.¹

In plant designed especially for the production of "*flowers of sulphur*," the condensing chambers may be of protected sheet iron and contain an arrangement of condensing surfaces, the entrained molten sulphur being separated by a baffle.² The modern production of finely ground sulphur has lessened the demand for sublimed sulphur, although the latter is considered more suitable for vulcanisation and agricultural purposes.

"*Chemically pure*" sulphur can be prepared from the foregoing products either by filtering whilst molten through glass wool and subsequently distilling under reduced pressure,³ or by repeated distillation in a current of pure carbon dioxide.⁴ For the removal of organic impurities it is sufficient to heat the sulphur for a period a little below its normal boiling-point.

Applications of Sulphur.—Much sulphur is consumed in the manufacture of matches, being applied in the form of phosphorus sulphide as a constituent of the heads of common friction matches, whilst on the Continent the wooden splints have frequently been treated with sulphur to facilitate the passage of the flame from the head to the remainder of the match. Large quantities of sulphur are also required for the production of gunpowder and fireworks; for these purposes finely divided sulphur is necessary, but "*flowers of sulphur*" is not suitable on account of its liability to contain traces of sulphuric acid, due to atmospheric oxidation, which would render its use dangerous.

Sulphur is applied, commonly in the powdered form or as "*flowers of sulphur*," to medicinal purposes, and also agriculturally as a dust or dressing to check fungoid diseases of certain plants, especially the vine.⁵ The toxic properties of sulphur have not been fully elucidated and are variously ascribed to reduction to hydrogen sulphide, oxidation to polythionic acids, or to the vapour of the element itself, produced by slow vaporisation.⁶ If adsorbed pentathionic acid be removed from

¹ *German Patent*, 451796 (1926).

² See, for example, White, *Chem. Met. Eng.*, 1928, 35, 355.

³ Threlfall, Brearley and Allen, *Proc. Roy. Soc.*, 1894, 56, 32; Wilkinson, *American Patent*, 1560926 (1925).

⁴ Vogel and Partington, *Trans. Chem. Soc.*, 1925, 127, 1514.

⁵ Marcille, *Compt. rend.*, 1911, 152, 780. See also Fife, *Soil Sci.*, 1926, 21, 245; Neller, *Ind. Eng. Chem.*, 1926, 18, 72; Williams and Young, *ibid.*, 1929, 21, 359; Marsh, *J. Pomology*, 1929, 7, 237.

⁶ See Williams and Young, *loc. cit.*; Marsh, *loc. cit.*; Tucker, *Ind. Eng. Chem.*, 1929,

sulphur by means of ammonia, the sulphur loses its toxicity but regains it if suspended in water and exposed to air.¹

The element has a definite fertilising action² which is exerted in two ways: (1) It supplies sulphuric acid by bacterial oxidation, the presence of the acid increasing the availability of certain mineral constituents in the soil, such as alkalis, ferric oxide, alumina and phosphates. (2) It facilitates the work of the ammonia and nitrifying bacteria, thus placing larger supplies of nitrogen at the disposal of the plants. But although such action may be beneficial in some soils it is equally harmful in others, and sulphur should not be applied to a soil already acid.³

Many important inorganic compounds of sulphur, such as carbon disulphide, sulphur chloride, phosphorus sulphide, vermilion and "Mosaic gold," are manufactured from their constituent elements, and considerable quantities of free sulphur are also used in the preparation of certain organic dyes, the colouring matter Primuline probably being the best known "sulphur dye," Methylene Blue and Thioindigo being other examples of this class of dyestuffs. The vulcanisation of rubber⁴ also calls for the use of sulphur and sulphur compounds. For this purpose, one of the following methods is usually employed: (1) The rubber is mixed with powdered sulphur and heated to a temperature of 135° to 160° C.; in the presence of a suitable accelerator a considerably lower temperature may be employed. (2) The rubber is dipped into a solution of sulphur chloride in a suitable inert solvent such as carbon disulphide, or is exposed to the vapour of such a solution; this method is restricted to thin material or surface treatment. (3) The rubber, either dry or in solution, e.g. in benzene, is treated successively with sulphur dioxide⁵ and hydrogen sulphide (see p. 115). The product obtained by the first process may be soft or hard (ebonite) according to the proportion of sulphur going into combination. Various unsaturated oils, e.g. the so-called "drying oils," can be "vulcanised" by similar means so as to yield elastic solids possessing, however, very little tensile strength. By heating with sulphur in a somewhat similar manner tar can be rendered harder and therefore more useful for many purposes. Resinous condensation products of high melting-point and considerable hardness may be obtained by heating homologues or substituted derivatives of phenol with sulphur in the presence of a basic catalyst.⁶

Sulphur has recently been described⁷ as a valuable agent for

21, 44. For the physiological action of sulphur, see Földes, *Chem. Zentr.*, 1928, ii., 464; Pincus, *ibid.*, p. 1347; Marston and Robertson, *Council Sci. Res. Australia*, 1928, Bull. 39, 5.

¹ Young and Williams, *Science*, 1928, 67, 19.

² Nicolas, *Compt. rend.*, 1921, 172, 86; Lipman, Waksman, and Joffe, *Soil Sci.*, 1921, 12, 475; MacIntire, Gray and Shaw, *ibid.*, 1921, 11, 249; *J. Ind. Eng. Chem.*, 1921, 13, 310; Simon and Schollenberger, *Soil Sci.*, 1925, 20, 443; Guittouneau, *Compt. rend.*, 1926, 182, 661.

³ See also McKibbin, *Md. Agric. Exp. Sta. Bull.*, 1928, No. 296, 95; Jones, *Soil Sci.*, 1928, 26, 447; Hengl and Reckendorfer, *Bied. Zentr.*, 1928, 57, 536.

⁴ See Twiss, *J. Soc. Chem. Ind.*, 1917, 36, 782. Also H. P. Stevens, *ibid.*, 1919, 38, 192 T; 1928, 47, 37 T; with W. H. Stevens, *ibid.*, 1929, 48, 65 T.

⁵ Peachey and Shipsey, *J. Soc. Chem. Ind.*, 1921, 40, 5 T; Bedford and Schrell, *J. Ind. Eng. Chem.*, 1922, 14, 25.

⁶ Ges. für Chem. Ind. in Basel, *Swiss Patents*, 105855-S (1922); cf. Imray, *British Patent*, 186107 (1921).

⁷ Kobbé, *Chem. and Met. Eng.*, 1926, 33, 354.

impregnating wood. The absorption of molten sulphur by the wood preserves and strengthens it and gives it acid-resisting properties.

Amongst other applications may be mentioned the use of free sulphur in the manufacture of Ultramarine and the occasional conversion of the element into thiosulphates (see p. 198), sulphurous acid or sulphur dioxide (p. 108) and sulphuric acid (p. 150).

THE ALLOTROPY OF SULPHUR.

Ever since the recognition of allotropy amongst the elements, sulphur has occupied the position of being the most marked example. So complex is the behaviour of the element, however, that even at the present time a complete interpretation is not possible.

Changes in the Vaporous State.—Even in the state of vapour the problem presented by the behaviour of sulphur is far from simple. As soon as moderately accurate results for vapour density were available it became clear that with elevation of temperature from the boiling-point upwards the vapour molecules undergo reduction in weight, approaching the condition S_2 when near 1000°C. , whilst in the neighbourhood of the boiling-point, under atmospheric pressure, the vapour density attains a value almost corresponding with the molecule S_8 ,¹ which is the molecular condition of ordinary dissolved sulphur (see the following). More recent experiments have confirmed these results and have shown that even at the boiling-point the S_8 molecules of sulphur vapour are accompanied by smaller molecules, the proportion of the latter gradually increasing as the temperature rises until when near 900°C. only S_2 molecules are present.² Above 1700°C. the S_2 molecules begin to suffer incipient dissociation into single atoms and at 2070°C. the vapour density corresponds to a molecular weight of only 50, indicating that the vapour contains a considerable percentage of monatomic molecules.³ From the pressure resulting during the explosion of "detonating gas" ($2\text{H}_2 + \text{O}_2$) mixed with hydrogen sulphide it has been calculated that at 2450°C. , under atmospheric pressure, 50 per cent. of the diatomic sulphur molecules undergo further dissociation into single atoms.⁴

Vapour density experiments conducted under reduced pressure and at temperatures below the normal boiling-point of sulphur⁵ have shown that under such conditions sulphur vapour gradually approaches the octa-atomic condition as the temperature is lowered; this is indicated by the following figures:

¹ Deville and Troost, *Compt. rend.*, 1863, 56, 891; Biltz, *Zeitsch. physikal. Chem.*, 1888, 2, 920.

² Ramsay, *Zeitsch. physikal. Chem.*, 1880, 3, 67; Riecke, *ibid.*, 1890, 6, 268, 430; *Ber.*, 1890, 23, 724; Troost, *Compt. rend.*, 1878, 86, 1294; Biltz, *Zeitsch. physikal. Chem.*, 1888, 2, 920; 1897, 19, 425; *Ber.*, 1888, 21, 2013; 1901, 34, 2490; *Monatsh.*, 1901, 22, 627; Biltz and Meyer, *Ber.*, 1889, 22, 725; *Zeitsch. physikal. Chem.*, 1889, 4, 249; Meyer and Meyer, *Ber.*, 1879, 12, 1115; Scott, *Ann. Phys. Chem. Beibl.*, 1888, [iii.], 12, 411.

³ Biltz and Meyer, *loc. cit.*; Nernst, *Zeitsch. Elektrochem.*, 1903, 9, 626; von Wartenberg, *Zeitsch. anorg. Chem.*, 1907, 56, 320.

⁴ Budde, *Zeitsch. anorg. Chem.*, 1912, 78, 189.

⁵ Troost, *Compt. rend.*, 1878, 86, 1396; Bleier and Kohn, *Monatsh.*, 1900, 21, 575; *Ber.*, 1900, 33, 50. See also Schall, *Ber.*, 1890, 23, 1704; 1900, 33, 484.

Temperature, ° C.	Vapour Density (Air=1).	Molecular Weight.	Apparent Number of Atoms per Molecule.
310	8.26	237.9	7.44
262	8.34	240.1	7.50
236	8.52	245.2	7.66
212	8.67	249.6	7.80
193	8.73	251.1	7.85

The gradual disintegration of the S_8 molecule at higher temperatures can also be observed by the alteration of the vapour density when the pressure is reduced and the temperature allowed to remain constant.¹ Indeed, this method of examining the alteration in the molecular condition of sulphur vapour has yielded important information. At one time it was believed that the S_8 molecule disintegrated in successive stages to S_6 and S_4 before reaching the diatomic condition, but it now appears probable that there is only one intermediate stage, namely S_6 , which form of sulphur vapour appears to stand in close relationship with one of the forms of liquid sulphur, namely S_μ (see later).

External evidence is available in confirmation of the remarkable molecular alteration in sulphur vapour. Near the boiling-point sulphur vapour is orange-red, but the colour fades to a straw-yellow as the temperature is raised; indeed, above 1000°C. the vapour is said to become colourless and on reaching 1400°C. to assume a pale blue tint.² The absorption spectrum of sulphur vapour³ has been examined over the range 400° to 1200°C. , and it is found that absorption increases as the temperature is raised to about 650°C. but above this temperature it decreases as the vapour becomes more and more transparent. This agrees with the view that the dissociation $S_8 \rightarrow S_2$ is not direct, but that molecules of intermediate complexity and of greater absorptive power than S_2 are formed and in turn dissociated. No further change is observable above 900°C. The fluorescence⁴ observable in the vapour under reduced pressures also shows variations indicative of the alteration in molecular condition.

Allotropy in the Liquid State.—When the temperature of sulphur is gradually raised from the melting-point, a notable change is observable near 160°C. , the colour of the liquid beginning to deepen, whilst the fluidity commences to decrease.⁵ The occurrence of this change, or at

¹ Biltz and Preuner, *Ber.*, 1901, 34, 2490; Preuner, *Zeitsch. physikal. Chem.*, 1903, 44, 733; Preuner and Schupp, *ibid.*, 1909, 68, 129; Preuner and Brockmüller, *ibid.*, 1912, 81, 129. See also Bodenstein, *Zeitsch. physikal. Chem.*, 1899, 29, 315; Milbauer, *Ann. Chim. Phys.*, 1907, [viii.], 10, 125; Stafford and von Wartenberg, *Zeitsch. physikal. Chem.*, 1911, 77, 66.

² Paternò and Mazzucchelli, *Atti R. Accad. Lincei*, 1907, [v.], 16, i., 465; Howe and Hamner, *J. Amer. Chem. Soc.*, 1898, 20, 757.

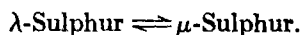
³ Salet, *Compt. rend.*, 1871, 73, 559; Gernez, *ibid.*, 1872, 74, 804; Graham, *Proc. Roy. Soc.*, 1910, [A], 84, 311; Dobbie and Fox, *ibid.*, 1919, [A], 95, 484; Norrish and Rideal, *Trans. Chem. Soc.*, 1924, 125, 2070.

⁴ Diestelmeier, *Zeitsch. wiss. Photochem.*, 1915, 15, 18; Steubing, *Physikal. Zeitsch.*, 1913, 14, 887.

⁵ Pisati, *Gazzetta*, 1877, 7, 337; Brunhes and Dussy, *Compt. rend.*, 1894, 118, 1045; Schann, *Annalen*, 1899, 308, 18; Smith and Holmes, *Zeitsch. physikal. Chem.*, 1905, 52, 802; *J. Amer. Chem. Soc.*, 1905, 27, 797.

least its extent, is dependent on the previous history of the sulphur, for it may be delayed or be much less marked if the sulphur is of a high degree of purity; the reason for this is to be sought in the catalytic influence of certain impurities (see p. 18). Under ordinary conditions the viscosity attains a maximum between 170° and 220° C., the colour being then a very deep brown. Further rise in temperature causes a partial restoration of the fluidity, but the deep colour is retained. These striking and exceptional changes are attributed to the presence of three different forms of sulphur in the liquid, and careful investigations of the phenomena have been made, especially by A. Smith and various collaborators.¹

A full interpretation of the results of the investigations is rendered difficult by the complications introduced by external influences such as those due to certain impurities which it is almost impossible to exclude. It is clearly recognisable, however, that the abnormal behaviour is due mainly to the existence of two distinct modifications of molten sulphur, side by side; these are commonly distinguished as λ -sulphur and μ -sulphur, and the equilibrium between them at any temperature may be expressed



The position of the equilibrium varies with the temperature, the proportion of μ -sulphur being less at lower temperatures; near the melting-point the proportion of μ -sulphur approximates to 4 per cent., and the maximum at higher temperatures generally does not much exceed 40 per cent. It was at one time believed that rapid cooling could effect the separation of molten sulphur into two distinct layers,² but careful examination has shown the lack of homogeneity to be due only to temperature differences caused by the viscosity and the poor thermal conductivity of the liquid; the two modifications are completely miscible in the liquid state.³

By rapidly cooling the fluid mixture it is possible to minimise the readjustment of the equilibrium and to attain a solid condition in which the original proportions of the mixture are approximately retained; in the solid state the allotropic change is so very slow as to allow careful and fairly prolonged examination of the mixture. It is then found that the normal mobile liquid constituent (S_λ) has given rise to crystalline sulphur, soluble in carbon disulphide, whereas the dark-coloured viscous constituent (S_μ) has produced an amorphous solid, insoluble in this solvent⁴ (see also p. 19). A rough analysis of molten sulphur in

¹ Brodie, *Proc. Roy. Soc.*, 1856, 7, 24; *Compt. rend.*, 1875, 80, 515; Magnus and Weber, *Ann. Phys. Chem.*, 1856, [ii.], 99, 145; Deville, *Compt. rend.*, 1848, 26, 117; Berthelot, *J. prakt. Chem.*, 1857, 71, 360; Küster, *Zeitsch. anorg. Chem.*, 1898, 18, 369; Schaum, *Zeitsch. physikal. Chem.*, 1900, 33, 382; Kruyt, *ibid.*, 1908, 64, 513; 1909, 65, 486; 67, 321; 1913, 81, 726; Smith and others, *ibid.*, 1903, 42, 489; 1905, 52, 602; 1906, 54, 257; 1907, 61, 200; 1911, 77, 681; also *Proc. Roy. Soc. Edin.*, 1902, 24, 299; 1905, 25, 588, 590; 1906, 26, 352; Carson, *J. Amer. Chem. Soc.*, 1907, 29, 499; Lewis and Randall, *ibid.*, 1911, 33, 476; Kellas, *Trans. Chem. Soc.*, 1918, 113, 903.

² Smith, *Proc. Roy. Soc. Edin.*, 1905, 25, 588; Hoffmann and Rothe, *Zeitsch. physikal. Chem.*, 1906, 55, 113; Erdmann, *Annalen*, 1908, 362, 133.

³ Smits and Leeuw, *Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 461; Leeuw, *ibid.*, 1912, 15, 584; Smits, *Zeitsch. physikal. Chem.*, 1913, 83, 221.

⁴ Wigand, *Zeitsch. physikal. Chem.*, 1908, 63, 273; 1910, 72, 752; 75, 235; Smith and Holmes, *ibid.*, 1903, 42, 489; 1906, 54, 257; Hammett, Cousins and Langford, *J. Chem. Soc.*, 1928, p. 797.

this way becomes possible. Recent experiments,¹ however, suggest that the insoluble μ -sulphur is not present as such in liquid sulphur, but makes its appearance, possibly as a gel, only when the liquid solidifies.

If sulphur is heated to 180° C. and then cooled, it becomes more soluble in carbon disulphide; also a saturated solution of sulphur chloride in toluene at the ordinary temperature will, after being heated to the neighbourhood of 180° C. and cooled again, dissolve yet more sulphur. These observations led to the discovery of a third modification in molten sulphur. This form of sulphur, distinguished as π -sulphur, is formed to some extent when ordinary sulphur is heated to 125° C. The optimum temperature for its formation is near 180° C., when the liquid contains approximately 6.5 per cent. of S_π with 20.5 per cent. of S_μ and 73 per cent. of S_λ . π -Sulphur exists as a definite and distinct modification both in the liquid and the solid state.² It is especially notable on account of its deep orange-yellow colour, which is also seen in its solutions, a fairly concentrated solution in carbon disulphide having the colour of a concentrated aqueous solution of potassium dichromate. π -Sulphur is unstable at the ordinary temperature, its transformation being accelerated by ammonia solution and also by the influence of light; the products of its transformation are octahedral sulphur and some insoluble sulphur. A suggestion that π -sulphur has a molecular weight corresponding to S_4 needs further experimental confirmation.

The existence of yet another form of sulphur, designated ϕ -sulphur, formed together with π -sulphur but of a somewhat paler colour, although deeper than octahedral or monoclinic sulphur, is also suspected (see p. 26).

The presence of the μ - and π -modifications of sulphur dissolved in molten λ -sulphur naturally causes a depression of the freezing-point of the latter, and from the magnitude of this effect it has been possible to demonstrate the probability of a molecular weight corresponding to S_6 for the dark brown μ -allotrope, a result which is of especial interest as correlating this form of liquid sulphur with the hexatomic sulphur believed to occur in sulphur vapour (see before).³

Kellas,⁴ however, from measurements of the surface tension of liquid sulphur, maintains that between 115° and 160° C. at least 95 per cent. of mobile sulphur is represented by the formula S_6 , and that above 160° C. polymerisation occurs, resulting in the formation of S_{18} or $(S_6)_3$ molecules, which are stable nearly up to the boiling-point.

On account of the variability of the proportions of λ -sulphur, μ -sulphur and π -sulphur in the liquid, the solidifying-point of molten sulphur is not constant, but may range from 114° to 117° C. or even more widely. The freezing-point of pure λ -sulphur can be determined by calculation, the result, 119.25° C., almost coinciding with the temperature

¹ Hammick and Zvegintzov, *J. Chem. Soc.*, 1930, p. 273.

² Aten, *Zeitsch. physikal. Chem.*, 1912, 81, 257; 1913, 83, 442; 86, 1; 1914, 88, 321; *Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 572; 1918, 20, 824. See also Gaubert, *Compt. rend.*, 1916, 162, 554; Beckmann, Paul and Liesche, *Zeitsch. anorg. Chem.*, 1918, 103, 189.

³ Smith, *Proc. Roy. Soc. Edin.*, 1902, 24, 299; Smith and Carson, *Zeitsch. physikal. Chem.*, 1911, 77, 661; Beckmann, *Sitzungsber. K. Akad. Wiss. Berlin*, 1913, 686. See also Gernez, *Compt. rend.*, 1876, 82, 1153; 1883, 97, 1298; Dussay, *ibid.*, 1896, 123, 305; Duhem, *Zeitsch. physikal. Chem.*, 1897, 23, 224.

⁴ Kellas, *loc. cit.*

119.2° C. observed in the crystallisation of pure λ -sulphur and with the ideal melting-point of pure monoclinic sulphur.¹

Certain substances, especially ammonia, exert a catalytic influence on the two changes involved in the foregoing equilibrium, greatly facilitating the attainment of the equilibrium; on this account the presence of a little ammonia, or an organic base such as aniline or pyridine, causes soluble sulphur to be formed almost exclusively on solidification. On the other hand, several other substances, *e.g.* sulphur dioxide² (or gases such as air or oxygen which can give rise to sulphur dioxide), halogen hydracids, phosphoric acid and organic acids,³ behave as negative catalysts, and when molten sulphur is cooled, cause the μ -sulphur to persist in a quantity in excess of the equilibrium proportion at lower temperatures, so that these substances raise the percentage of insoluble sulphur in the solidified mass. It is possible that the action of ammonia is merely due to its power of removing sulphur dioxide, traces of which are usually present in ordinary sulphur. Iodine not only exerts a catalytic effect of the same type as sulphur dioxide, but also causes an increase in the proportion of μ -sulphur in the liquid.⁴

For the foregoing reasons it is seldom possible to obtain reproducible viscosity values for a given sample of sulphur. If, however, pure gas-free sulphur is prepared by distillation first in carbon dioxide and then in high vacuum, reliable values may be obtained. For such sulphur, protected from exposure to air, it has been found⁵ that the viscosity between 168° and 169° C., the interval of high viscosity variation, lies on the same curve whatever the previous thermal treatment of the sample may have been.

Exposure to bright light, for example to a concentrated beam of the sun's rays or to the electric arc, produces an increase in the proportion of the μ -modification in liquid sulphur.⁶ A similar effect is observable even in solution; if a solution of sulphur in carbon disulphide is similarly illuminated, insoluble sulphur gradually separates; the reverse change occurs in the dark.⁷ The conclusion can therefore be drawn that in solution also there is an equilibrium between the λ - and μ -forms at the ordinary temperature, but that except under the influence of light the concentration of μ -sulphur is not sufficient to cause separation of the corresponding solid.

In spite of these allotropic changes, molten sulphur under certain conditions can be successfully used as a cryoscopic solvent. Soon after having been melted, the freezing-point of the liquid may be as high as 119° C., but after keeping for some hours at a temperature just above

¹ Smith and Holmes, *loc. cit.*; Kruyt, *Zeitsch. physikal. Chem.*, 1913, 81, 726; 84, 498.

² Smith, *Proc. Roy. Soc. Edin.*, 1906, 26, 352; Beckmann and Platzmann, *Zeitsch. anorg. Chem.*, 1918, 102, 201. According to Moissan (*Ann. Chim. Phys.*, 1907, [viii.], 10, 433), sulphur, when fused after exposure to moist air, frequently contains sulphur dioxide and hydrogen sulphide in small quantities.

³ For a viscosimetric examination of the influence of certain organic substances (*s.g.* phenol, camphor) on the transformation temperature, see Mondain-Monval and Schneider, *Compt. rend.*, 1928, 186, 751.

⁴ Smith and Carson, *Proc. Roy. Soc. Edin.*, 1906, 26, 352; *Zeitsch. physikal. Chem.*, 1907, 61, 200.

⁵ Farr and Macleod, *Proc. Roy. Soc.*, 1928, [A], 118, 534.

⁶ Wigand, *loc. cit.*; also *Zeitsch. physikal. Chem.*, 1909, 65, 442; 1911, 77, 423; 78, 208.

⁷ Leliedam, *Compt. rend.*, 1870, 70, 182; Berthelot, *ibid.*, 1870, 70, 941; Schaub, *Annalen*, 1899, 308, 18; Rankin, *J. Physical Chem.*, 1907, 11, 1.

the melting-point, the freezing-point falls to 114.5°C. , and in this condition the sulphur is suitable for cryoscopic determinations,¹ the constant K being 213.

When molten sulphur is rapidly cooled from the neighbourhood of 400°C. , an amber-coloured semi-elastic mass of density about 1.9 is obtained. This so-called "*plastic sulphur*" is in reality an under-cooled liquid sulphur and gradually hardens or solidifies to a mixture of soluble and insoluble sulphur,² the change being hastened by kneading or by heating in boiling water. The rate of hardening is naturally dependent on the relative proportions of the two modifications and so will be influenced by the extent of the sudden fall in temperature; e.g. the higher the temperature of the sulphur as it is poured into cold water, the slower the solidification.³ If the cooling is still more rigorous, as by immersion in liquid air, a hard mass may be obtained,⁴ which on warming assumes the elastic character, possibly in greater degree, and finally solidifies in the usual manner. In its general character it will be seen that "*plastic sulphur*" resembles materials like glass or "*barley sugar*" which have been produced by cooling liquids much below their normal temperatures of crystallisation without any sharp change in state.

As is to be expected the equilibrium between the two above-mentioned forms of liquid sulphur affects other properties in addition to the colour and the viscosity. Thus, the electrical conductivity⁵ and the surface tension⁶ of molten sulphur exhibit abnormal variation with alteration in temperature; also the solubility curves for λ -sulphur and μ -sulphur in high-boiling solvents such as triphenylmethane are quite distinct, the solubility of the former increasing and that of the latter decreasing with rise of temperature; the respective coefficients of expansion are also quite independent.⁷ The reactivities of the two forms towards rubber are practically equal.⁸

More or less drastic modifications⁹ of the above view of the nature of molten sulphur have been suggested, but none appears to be supported by sufficient evidence to deserve acceptance.

Allotropy in the Solid State.—When molten sulphur is allowed to solidify, the modifications present give rise to corresponding solid forms, the liquid λ -sulphur producing crystalline sulphur (rhombic, monoclinic or nacreous, according to the conditions), whilst the deep

¹ Beckmann and Platzmann, *Zeitsch. anorg. Chem.*, 1918, 102, 201.

² Smith, *Proc. Roy. Soc. Edin.*, 1905, 25, 590.

³ Kastle and Kelley, *Amer. Chem. J.*, 1904, 32, 483. For stress-strain curves for plastic sulphur, see Strong, *J. Physical Chem.*, 1928, 32, 1225.

⁴ von Weimarn, *Zeitsch. Chem. Ind. Kolloide*, 1910, 6, 250; Brodie, *Proc. Roy. Soc.*, 1854, 7, 24.

⁵ Pigulewski, *J. Russ. Phys. Chem. Soc.*, 1912, 44, *Phys. Part*, 105; Wigand, *Ber. deut. physikal. Ges.*, 1908, 6, 495; Pisati, *Gazzetta*, 1877, 7, 357; Zickendraht, *Ann. Physik*, 1906, [iv.], 21, 141.

⁶ Capelle, *Bull. Soc. chim.*, 1908, [iv.], 3, 764; Rudge, *Proc. Cambridge Phil. Soc.*, 1911, 16, i, 55; Kellas, *loc. cit.* See also Rotunjanz, *Zeitsch. physikal. Chem.*, 1908, 62, 609.

⁷ Smith, *Proc. Roy. Soc. Edin.*, 1905, 25, 588.

⁸ Twiss, *J. Soc. Chem. Ind.*, 1917, 36, 787; *Ann. Reports, Soc. Chem. Ind.*, 1919, p. 327; *Trans. Inst. Rubber Ind.*, 1928, 3, 386; Twiss and Thomas, *J. Soc. Chem. Ind.*, 1921, 40, 48 T. See also van Iterson, *Comm. Netherland Govt. Inst. Rubber Ind.*, 1916, 7, 257; Stoll, *Rubber Age, U.S.A.*, 1925, 17, 418; Dannenberg, *Kautschuk*, 1927, pp. 104, 128; Scholz, *ibid.*, 1927, pp. 101, 127.

⁹ See Erdmann, *Annalen*, 1908, 362, 133; Quincke, *Ann. Physik*, 1908, [iv.], 26, 625.

brown viscous μ -sulphur yields an amorphous pale yellow solid which is very sparingly soluble (generally described as "insoluble") in carbon disulphide and the other common solvents for sulphur.¹ This amorphous form of sulphur, which is frequently termed γ -sulphur, has no definite melting-point and so may be regarded as "undercooled" μ -sulphur. As the crystalline forms of sulphur are commonly obtained by separation from a melt containing some μ -sulphur, crystalline sulphur ordinarily contains an appreciable quantity of insoluble γ -sulphur in a state of solid solution (see p. 21). Mention has already been made of the formation of γ -sulphur as an insoluble powder when a carbon disulphide solution of sulphur is exposed to light.

Crystalline Forms of Sulphur.

The power of sulphur to crystallise in different forms was first recognised in 1823 by Mitscherlich,² who described the rhombic and prismatic varieties. The classification of the chief crystalline forms was completed by Muthmann,³ who distinguished them by Roman numerals.

Sulphur I. Rhombic, Octahedral or α -Sulphur.—This is the form commonly occurring in nature.⁴ On account of the presence of a small but variable quantity of the μ -modification of liquid sulphur (p. 16) and also S_2 in molten sulphur, the freezing-point of the latter is lacking in constancy and is dependent on the previous history of the liquid; crystallisation of molten sulphur generally gives rise to sulphur II. If, however, sulphur (preferably recrystallised from carbon disulphide and so containing a reduced proportion of γ - or μ -sulphur) is melted in a flask fitted with a cork carrying a zigzag glass tube, the contents of the flask may be cooled rapidly to 95° C. and then slowly to 90° C. before spontaneous crystallisation begins. By inverting the flask before solidification is complete, the octahedral crystals (sulphur I.) which form at the bottom of the flask may be examined, whilst the remainder of the sulphur is retained in the neck of the flask by the plug of solid sulphur formed in the bent outlet tube. Undercooled liquid sulphur can also be made to separate in the octahedral form by the addition of a crystal of this type, but the result is rendered more certain by working at a temperature below 95.5° C.⁵

Crystallisation of sulphur at the ordinary temperature from solution, e.g. from carbon disulphide, yields octahedral crystals which differ from the crystals obtained by the solidification of molten sulphur in that the proportion of γ - and π -sulphur, present in solid solution, is less. Octahedral crystals of sulphur may be prepared at the ordinary temperature also by the gradual atmospheric oxidation of a solution of

¹ Deville, *Compt. rend.*, 1848, 26, 117; Brodie, *Proc. Roy. Soc.*, 1854, 7, 24; Knapp, *J. prakt. Chem.*, 1848, [ii.], 43, 305; Chapman Jones, *Chem. News*, 1880, 41, 244; Küster, *Zeitsch. anorg. Chem.*, 1898, 18, 365; Brunhes and Dussy, *Compt. rend.*, 1894, 118, 1045; Dussy, *ibid.*, 1896, 123, 305; Malus, *ibid.*, 1900, 130, 1708; *Ann. Chim. Phys.*, 1891, [vi.], 24, 491; Wigand, *Zeitsch. physikal. Chem.*, 1909, 65, 442; 1910, 75, 235; Smith, *Proc. Roy. Soc. Edin.*, 1905, 25, 590, etc. (see pp. 26-28).

² Mitscherlich, *Ann. Chim. Phys.*, 1823, 24, 264.

³ Muthmann, *Zeitsch. Kryst. Min.*, 1890, 17, 336.

⁴ Ilsovay, *Zeitsch. Kryst. Min.*, 1885, 10, 91. See also Erdmann, *ibid.*, 1903, 37, 282; Banfaldi, *Mem. Accad. Lincei*, 1927, [vi.], 2, 266.

⁵ Gernez, *Compt. rend.*, 1876, 84, 217.

hydrogen sulphide in pyridine¹ or by the much slower process of sublimation.²

The foregoing crystals belong to the rhombic system,³ the elements $a : b : c = 0.8188 : 1 : 1.9076$ being subject to slight variation. This slight inconstancy is doubtless due in part to the presence of a small variable percentage of γ - and π -sulphur (p. 17) in the crystals, this impurity also accounting for the various figures which have been given at different times for the density, the correct value at the ordinary temperature for pure octahedral sulphur probably lying between 2.03 and 2.06.⁴

The melting-point of octahedral sulphur is influenced in a similar manner, and indeed the effect of these almost permanent impurities in the crystalline forms of sulphur has added to the difficulties of investigation. In the following table are given the ideal temperatures for the change of state of the various forms, together with the temperatures as commonly observed with the forms as usually obtained;⁵ the ideal temperatures can be approached only with specimens prepared with extreme care.

	Ideal Temperature, ° C.	Natural Temperature, ° C.	Percentage of "Impurity" present in latter case.
S. I.	Freezing-point 112.8	110.2	3.4
S. II.	„ 119.2	114.5	3.6
S. III.	„ 106.8	103.8	3.1
S. I. \rightleftharpoons S. II.	Transformation 95.3	95.5	3.1

Octahedral sulphur is a brittle solid of hardness approximately 2.3; the colour is lemon-yellow at the ordinary temperature but darkens somewhat on warming, whilst at -50° C. it almost disappears, leaving the solid practically colourless;⁶ the refractive index for sodium light is 2.08,⁷ the mean specific heat is 0.176,⁸ and the coefficient of cubic

¹ Ahrens, *Ber.*, 1890, 23, 2708.

² Arzruni, *Zeitsch. Kryst. Min.*, 1884, 8, 338.

³ Tschermak, *Mineralogie*, 1897, 331; Kokscharow, *Min. Russ.*, 1874, 6, 368; Arzruni, *loc. cit.*; Molengraaf, *Zeitsch. Kryst. Min.*, 1888, 14, 43; Busz, *ibid.*, 1889, 15, 616; Dana, *Amer. J. Sci.*, 1886, [iii.], 32, 389.

⁴ Marchand and Scheerer, *J. prakt. Chem.*, 1841, 24, 129; Deville, *Compt. rend.*, 1847, 25, 857; Kopp, *Annalen*, 1855, 93, 129; Pisati, *Ber.*, 1874, 7, 361; Petersen, *Zeitsch. physikal. Chem.*, 1891, 8, 609; Arons, *Ann. Phys. Chem.*, 1894, [iii.], 53, 106; Hecht, *ibid.*, 1904, [iv.], 14, 1008.

⁵ Smith and Holmes, *Zeitsch. physikal. Chem.*, 1903, 42, 469; 1906, 54, 257; Smith and Carson, *Proc. Roy. Soc. Edin.*, 1906, 26, 352; *Zeitsch. physikal. Chem.*, 1911, 77, 661; Kruyt, *ibid.*, 1908, 64, 513; 1909, 65, 486; 1909, 67, 321; 1913, 81, 726; 1913, 84, 498; *Proc. K. Akad. Wetensch. Amsterdam*, 1913, 15, 1228; Nernst, *Zeitsch. physikal. Chem.*, 1913, 83, 546; Wigand, *ibid.*, 1909, 65, 442; 1910, 75, 235.

⁶ Schönbein, *J. prakt. Chem.*, 1852, 55, 161.

⁷ Arons, *loc. cit.*; Schrauf, *Zeitsch. Kryst. Min.*, 1890, 18, 113; Becquerel, *Ann. Chim. Phys.*, 1877, [v.], 12, 5.

⁸ Mondain-Monval, *Compt. rend.*, 1926, 182, 58; cf. Bunsen, *Ann. Phys. Chem.*, 1870, [ii.], 141, 1; Wiebe, *Ber.*, 1879, 12, 790; Silvestri, *Gazzetta*, 1873, 3, 578; Hecht, *Ann. Physik*, 1904, [iv.], 14, 1008; Kurbatoff, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 311; Forch and Nordmeyer, *Ann. Physik*, 1906, iv., 20, 423.

expansion approximately 0.00022 at 20° C.¹ The plasticity and deformability are not appreciably increased by heating at temperatures up to 280° C. under pressures of 1000 to 19,600 kgm. per sq. cm.; under 19,800 kgm. per sq. cm., octahedral sulphur melts at 268° C.²

When a sphere cut from a crystal of rhombic sulphur is allowed to vaporise at 100° C., plane surfaces develop which correspond to the most important crystal faces.³

Carbon disulphide is an excellent solvent for rhombic sulphur, the proportions soluble in 100 parts by weight of the solvent at different temperatures being given in the following table; the highest temperature is the boiling-point of the saturated solution under ordinary atmospheric pressure.⁴

Temperature, ° C.	Sulphur Dissolved (Parts by Weight).	Temperature, ° C.	Sulphur Dissolved (Parts by Weight).
—11	16.5	38	94.6
0	24.0	48.5	146.2
15	37.1	55	181.8
22	46.0		

Methylene iodide, aniline, and benzyl chloride,⁵ especially when warm, are good solvents for sulphur; phenol is also fairly good. Other less powerful solvents are benzene,⁶ toluene, turpentine, chloroform, ether, alcohol and acetic acid.

Octahedral sulphur will form mixed crystals with selenium containing up to 35 per cent. of the latter, although no corresponding crystalline form of pure selenium has been isolated.⁷

Sulphur II. Prismatic, Monoclinic or β -Sulphur.—This is a variety of monosymmetric crystalline sulphur obtained ordinarily when sulphur crystallises at a temperature near the melting-point from the molten condition. The usual procedure in order to obtain distinct crystals is to allow molten sulphur to cool undisturbed until approximately one-half has crystallised, and then, after breaking the crust, to pour away the remaining liquid.⁸ Crystallisation by the rapid cooling of hot solutions (see the following) sometimes also yields this modification, although more frequently the variety obtained is S. III.⁹

The crystals consist of long slender needles belonging to the mono-

¹ Spring, *Bull. Acad. roy. Belg.*, 1881, [iv.], 2, 88; Wiebe, *loc. cit.*

² Rose and Mügge, *Nach. K. Ges. Wiss. Göttingen*, 1922, 10, 105. For the compressibility of rhombic sulphur, see Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1927, 62, 207.

³ Aminoff, *Zeitsch. Krist.*, 1927, 65, 632; *Chem. Zentr.*, 1928, i., 3.

⁴ Cosca, *Ber.*, 1868, 1, 138; Payen, *Compt. rend.*, 1852, 34, 456, 508. For the specific gravity of the solutions, see Pfeiffer, *Zeitsch. anorg. Chem.*, 1897, 15, 194. For the refractive index of the solutions, see Berghoff, *Zeitsch. physikal. Chem.*, 1894, 15, 431; Forch, *Ann. Physik*, 1902, [iv.], 8, 675.

⁵ von Bognaki, *J. Russ. Phys. Chem. Soc.*, 1905, 37, 92.

⁶ Kruyt, *Zeitsch. physikal. Chem.*, 1909, 65, 486.

⁷ Muthmann, *Zeitsch. Krist. Min.*, 1890, 17, 336.

⁸ Mitscherlich, *Annalen*, 1823, 24, 264; Brauns, *Verh. Ges. deut. Naturforsch. Aemte*, 1899, [ii.], 189; Silvestri, *Ber.*, 1876, 9, 292; Ogialoro, *Gazzetta*, 1884, 14, 30.

⁹ Muthmann, *loc. cit.*

clinic system, the parameters being $a : b : c = 0.99575 : 1 : 0.99983$; $\beta = 84.23^\circ$.¹ When prepared from molten sulphur this variety frequently possesses a pale amber colour, which is probably due in part to π -sulphur present as impurity, since crystals obtained from solution are of a much paler colour. The density,² 1.957 at 25°C ., is lower than that of the octahedral form, whilst the specific heat is higher. As is the case for sulphur I., the presence of variable proportions of π - and γ -sulphur in the crystals affects the constancy of the melting-point, so that whereas as usually prepared the melting-point is 114.5°C ., the melting-point of pure monoclinic sulphur should be 119.2°C . (see p. 21).

At the ordinary temperature the clear transparent crystals become opaque and friable, the change occupying from several hours to several days, and the alteration being due to a transformation into sulphur I.; if the needle crystals are not crushed they will retain their external form, although they are built up of minute octahedral crystals of the denser modification.³ Conversely, if octahedral sulphur crystals are maintained at a temperature within a few degrees of the melting-point, they gradually undergo conversion into sulphur II.

The transition point, at which ordinary sulphur I. and sulphur II. are in equilibrium, is at 95.5°C .,⁴ although if no trace of π - or γ -sulphur were present the temperature would be slightly lower (see p. 21). The afore-mentioned changes can occur a few degrees above or below the stated temperature and are considerably facilitated by contact with a little of the stable form; below 95.5°C . sulphur I. is the stable modification and sulphur II. is unstable, whilst above 95.5°C . and up to the point of fusion, the position is reversed. It is possible for each of the forms to exist for a considerable period within its unstable range of temperature, and it is obvious that but for this fact it would be impossible to determine the melting-point of octahedral sulphur.⁵ Specimens of sulphur II. may be kept unchanged for years between a microscopic slide and a cover glass.⁶ The actual velocity of the transformation is dependent on several factors,⁷ such as the temperature, the previous history of the sulphur, or in other words its content of γ - and π -sulphur, subjection to mechanical stress, and contact with the stable form or with a solvent; actinic light is said also to have an acceleratory influence on the transformation.⁸

Alteration of pressure affects the transformation in a more marked manner by actually influencing the transition temperature itself. Increase in pressure causes a rise in the transition temperature to an extent of approximately 0.05°C . per atmosphere. However, increase in pressure also raises the melting-point of each form, and the relation

¹ Muthmann, *loc. cit.*

² Marchand and Scheerer, *J. prakt. Chem.*, 1841, 24, 133; Deville, *Compt. rend.*, 1847, 25, 857; Rathke, *J. prakt. Chem.*, 1869, 108, 235; Petersen, *Zeitsch. physikal. Chem.*, 1891, 8, 609; Toepfer, *Ann. Phys. Chem.*, 1892, [iii.], 47, 173.

³ Threlfall, Brearley and Allen, *Proc. Roy. Soc.*, 1894, 56, 36.

⁴ Reichen, *Zeitsch. Kryst. Min.*, 1884, 8, 593; *Rec. Trav. chim.*, 1884, 2, 246; Tammann, *Ann. Phys. Chem.*, 1899, [iii.], 68, 683.

⁵ Gernez, *Compt. rend.*, 1884, 98, 810, 915; 1885, 100, 1343; 1909, 148, 1015.

⁶ Brauns, *Centr. Min.*, 1921, 225. See also Cohen, *Zeitsch. physikal. Chem.*, 1924, 109, 109.

⁷ Duham, *Zeitsch. physikal. Chem.*, 1897, 23, 254; Fraenkel and Goetz, *Zeitsch. anorg. Chem.*, 1925, 144, 45.

⁸ Brame, *L'Institut, Paris*, 1853, 305.

between the variations of the three temperatures with pressure is such that under 1288 atmospheres the transition temperature and the melting-points of the two forms coincide at $151^{\circ}\text{C}.$ ¹

These relationships are represented in an exaggerated manner in fig. 2. The lines AO, BC and OD represent the vapour pressures of sulphur I., sulphur II. and molten sulphur, respectively; OE and CF show the effect of pressure change on the melting-points of the two crystalline forms, whilst the effect of pressure on the transition temperature is indicated by BF.

Determination of the molecular weight by cryoscopic and ebullioscopic measurements in various solvents, including carbon disulphide, various

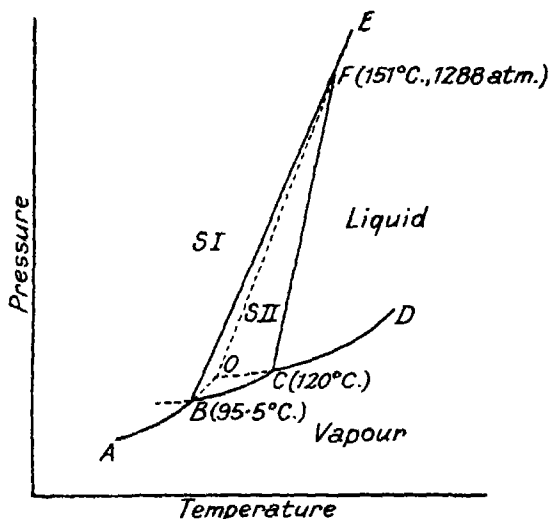


FIG. 2.—Relationship between Sulphur I. and Sulphur II.

hydrocarbons, and metallic chlorides such as antimonie or stannic chloride, indicates the value corresponding to S_8 both for octahedral and prismatic sulphur.² This is not surprising, because in the molten condition these two modifications of sulphur are identical, and their difference in crystalline form and other physical properties may be attributed to variation in the manner in which the octa-atomic molecules are grouped together in the crystal.

As is to be expected with modifications showing the mutual relationship described, the less stable form is more soluble in ordinary solvents; above $95.5^{\circ}\text{C}.$, therefore, the octahedral form is the more soluble, whilst below this temperature prismatic sulphur possesses the greater solubility. At the ordinary temperature the solubility ratio for most solvents is approximately 1.8 : 1.

Sulphur III. Nacreous Sulphur.—At least two other varieties of monoclinic sulphur are known to exist; the better known was discovered by D. Gernez in 1884, who, from the pearly lustre of the crystals,

¹ Tammann, *loc. cit.*; Roozeboom, *Rec. Trav. chim.*, 1887, 6, 315.

² Gloss, *J. Physical. Chem.*, 1899, 2, 421; Popoff, *J. Russ. Phys. Chem. Soc.*, 1903, 35, 642. See also p. 39.

gave it the name "nacreous sulphur."¹ This monosymmetric form of sulphur can be obtained by many different methods. Sulphur which has been heated in a glass tube to 150° C. and subsequently cooled slowly in a water-bath to 98° C. without crystallisation, can, by applying local cooling or by rubbing the interior of the tube with a glass rod already in the liquid, be made to give crystals of this modification.² Hot concentrated solutions of sulphur in carbon disulphide, benzene, toluene, turpentine and other solvents, prepared by heating sulphur with the solvent, preferably in a sealed tube, until no solid remains undissolved, generally deposit nacreous crystals on being rapidly cooled.³ Similar crystals can also be obtained by the precipitation of sulphur from carbon disulphide solution by the addition of ether,⁴ and also by subliming sulphur, e.g. from one watch glass into another acting as cover.⁵ Pure gas-free sulphur prepared by distillation first in a stream of carbon dioxide and then in high vacuum yields only nacreous sulphur on solidifying.⁶

Under suitable conditions, certain chemical reactions will give rise to nacreous sulphur; the most satisfactory result is obtained by allowing slow inter-diffusion of solutions of sodium thiosulphate and potassium hydrogen sulphate to occur.⁷ Another method involves the gradual decomposition of sulphur chloride or bromide by the vapour of water or methyl alcohol at the ordinary temperature.⁸ The decomposition of calcium polysulphides by hydrochloric acid,⁹ and of hydrogen persulphide by the addition of alcohol, ether, ethyl acetate or other organic solvents, also yields sulphur of the desired modification.

Nacreous sulphur forms clear, pale yellow (almost colourless), doubly refractive leaflets of the monoclinic class, $a : b : c = 1.06094 : 1 : 0.70944$; $\beta = 88.2^\circ$.¹⁰ The degree of pearly lustre is largely dependent on the method of preparation. This form of sulphur is unstable and tends to change more or less rapidly, without alteration in external form, into sulphur I., i.e. octahedral sulphur.¹¹ The natural melting-point is 103.8° to 103.9° C.,¹² but, on account of its tendency at this temperature to undergo conversion into sulphur II. (ordinary monoclinic sulphur), nacreous sulphur, when heated slowly, may give a melting-point approaching that of sulphur II. In any case the crystals contain small percentages of γ - and π -sulphur; the ideal melting-point for pure nacreous sulphur would approximate to 106.8° C. (see p. 21).¹³

¹ Gernez, *Compt. rend.*, 1883, 97, 1477; 1884, 98, 144; 1885, 100, 1584; *Ber.*, 1884, 17, 41; 1885, 18, 492. See also Maquenne, *Bull. Soc. chim.*, 1884, 41, 238; *Compt. rend.*, 1885, 100, 1490.

² Gernez, *loc. cit.*
³ Payen, *Compt. rend.*, 1852, 34, 456, 508; Bruhns and Muthmann, *Zeitsch. Kryst. Min.*, 1890, 17, 398; Deville, *Compt. rend.*, 1852, 34, 534, 561; Debray, *ibid.*, 1858, 46, 576; Gernez, *loc. cit.*; also *Zeitsch. Kryst. Min.*, 1886, 11, 189; Royer, *Compt. rend.*, 1859, 48, 845; Lehmann, *Zeitsch. Kryst. Min.*, 1877, 1, 128; d'Avallon, *Compt. rend.*, 1864, 58, 54; Bloxam, *Chem. News*, 1886, 53, 181.

⁴ Sabatier, *Compt. rend.*, 1885, 100, 1346.

⁵ Engelmann, *Zeitsch. Kryst. Min.*, 1899, 30, 605; Salomon, *ibid.*, 1899, 30, 605.

⁶ Farr and Macleod, *Proc. Roy. Soc.*, 1928, [A], 118, 534.

⁷ Gernez, *loc. cit.*

⁸ Cloëz, *Compt. rend.*, 1858, 46, 485; Bruhns and Muthmann, *loc. cit.*

⁹ Spica, *Zeitsch. Kryst. Min.*, 1886, 11, 409. See also Wetherell, *Amer. J. Sci.*, 1865, [ii.], 40, 330; Barilari, *Gazzetta*, 1878, 8, 178; Berthelot, *Ann. Chim. Phys.*, 1857, [iii.], 50, 376.

¹⁰ Salomon, *loc. cit.*

¹¹ See Kohlschütter, *Koll. Chem. Beihefte*, 1927, 24, 319.

¹² Farr and Macleod, *loc. cit.*

¹³ Kruyt, *Zeitsch. physikal. Chem.*, 1913, 81, 726.

Although no crystalline variety of selenium is known corresponding to nacreous sulphur, this modification of sulphur can form mixed crystals containing between 35 and 66 per cent. of selenium.¹

Sulphur IV. Tabular Sulphur.—This is another variety of monoclinic or monosymmetric sulphur which is exceedingly unstable and has, in consequence, been little investigated.¹ When the clear liquid obtained by saturating an alcohol solution of ammonium or sodium sulphide with sulphur is diluted with four times its bulk of alcohol and then allowed to stand at the ordinary temperature, nacreous sulphur (sulphur III.) separates. At temperatures below 14° C., however, e.g. at 5° C., the deposit consists of a mixture of nacreous sulphur with the fourth crystalline form, or may even consist entirely of the latter.

Other Crystalline Forms.—In addition to the foregoing crystalline modifications of sulphur, at least two others have been observed. When using boiling sulphur as the heating agent in the outer jacket of a Victor Meyer vapour density apparatus, Friedel,² in 1879, noticed the formation of very unstable *triclinic* crystals inside the upper part of the jacket; these crystals rapidly underwent change into ordinary octahedral sulphur. Various crystalline structures may be observed when sulphur condenses in droplets on a glass plate and solidifies.³ Such crystals are also unstable.

By extracting with chloroform the aqueous solution obtained by mixing concentrated solutions of sodium thiosulphate and hydrochloric acid at 10° C., a solution is obtained, which, after evaporating off the solvent chloroform, leaves rhombohedral orange-yellow crystals of sulphur.⁴ This form of sulphur is commonly known as *Engel's rhombohedral sulphur*, or S_ϕ . The crystals are usually prisms of specific gravity 2.135. Although it corresponds with the rhombohedral forms of selenium and tellurium,⁵ rhombohedral sulphur is very unstable and, in the course of a few hours, changes into a mixture of octahedral and insoluble sulphur.⁶

By crystallising sulphur from chloroform solution containing rubber as a thickening agent and a few drops of benzonitrile, two other forms, also claimed to be distinct allotropes, have been obtained,⁷ designated respectively ζ - and η -sulphur. Both forms are practically colourless and the crystals are doubly refracting; the former crystallises in rhombic plates and the latter in hexagonal plates.

Amorphous Sulphur.

"*Insoluble Amorphous Sulphur*" is produced, usually together with some sulphur soluble in carbon disulphide, by many reactions in which sulphur is set free. The slow decomposition of sulphur chloride or bromide by water, which may require several days for completion, gives a very stable form of insoluble sulphur.⁸ The action of mineral acids on

¹ Muthmann, *Zeitsch. Kryst. Min.*, 1890, 17, 336, 398.

² Friedel, *Bull. Soc. chim.*, 1879, 32, 114.

³ Whitaker, *J. Physical Chem.*, 1925, 29, 399.

⁴ Engel, *Compt. rend.*, 1891, 112, 866; *Ber.*, 1891, 24, 551; Aten, *Zeitsch. physikal. Chem.*, 1914, 88, 321.

⁵ Friedel, *Compt. rend.*, 1891, 112, 834, 866.

⁶ See also Gaubert, *ibid.*, 1916, 162, 554; Bichowsky, *J. Washington Acad. Sci.*, 1918, 9, 126.

⁷ Korinth, *Zeitsch. anorg. Chem.*, 1928, 174, 57.

⁸ Berthelot, *Compt. rend.*, 1857, 44, 318, 378; Cloëz, *ibid.*, 1858, 46, 485; 1858, 47, 819; Petersen, *Zeitsch. physikal. Chem.*, 1891, 3, 609.

solutions of thiosulphates and polythionates,¹ the oxidation of hydrogen sulphide by sulphurous acid² or concentrated sulphuric acid,³ the oxidation of hydrogen sulphide or metallic sulphides by nitric acid or halogens,⁴ and the incomplete combustion of sulphur compounds⁵ such as hydrogen sulphide or carbon disulphide, all yield some of this sparingly soluble sulphur. It is interesting to note that all these reactions occur in the presence of free acid which, as has been already mentioned, is favourable to the existence of μ -sulphur (p. 18).

In all probability the primary product when sulphur is precipitated by chemical action consists entirely of the insoluble γ -sulphur, but, as soon as formed, this begins to change rapidly into the more stable soluble crystalline form in a fine state of division. The presence of halogens retards this change, so that a concentrated solution of bromine or iodine, acting on a solution of a sulphide or polysulphide, will give a product containing a higher proportion of insoluble sulphur than will a more dilute solution. Hydrogen ions also exert a retarding effect, so that whereas the interaction of acetic acid or dilute hydrochloric acid with a solution of a thiosulphate or polysulphide yields a product entirely soluble in carbon disulphide, the precipitate obtained with concentrated hydrochloric acid contains a considerable proportion of insoluble γ -sulphur.⁶

"Flowers of sulphur" (see p. 12), when freshly prepared, commonly contains about 30 per cent. of insoluble sulphur, but this percentage may vary considerably.⁷ However, if sulphur vapour is condensed on the surface of cold water or especially on the surface of a cold aqueous solution of a mineral acid such as sulphuric acid, the proportion of the insoluble amorphous modification in the deposit may be so high as to render it the main constituent.⁸

The insoluble sulphur obtained by these various methods is somewhat inconstant in physical properties, but all the varieties are included under the designation γ -sulphur. They are generally loose amorphous powders of pale yellow colour, the density ranging from 1.85 to 2.05.⁹ They all have a tendency to change spontaneously into soluble crystalline sulphur, the change at 110° C. being accompanied by a slight evolution of heat.¹⁰ Contact with a cold aqueous solution of hydrogen sulphide or of an alkali sulphide has a marked accelerating effect on the change, as also has compression,¹¹ or heat-

¹ Berthelot, *loc. cit.*; Fordos and Gélus, *Ann. Chim. Phys.*, 1851, [iii.], 32, 385.

² Sobrero and Selmi, *Ann. Chim. Phys.*, 1850, [iii.], 28, 210; de Luca and Ubaldini, *Compt. rend.*, 1867, 64, 1200.

³ Berthelot, *loc. cit.*

⁴ Selmi, *J. Pharm. Chim.*, 1852, [iii.], 21, 418; Selmi and Missaghi, *Cimento*, 1855, 2, 381; W. R. H., *Chem. News*, 1876, 34, 68.

⁵ Berthelot, *loc. cit.*; see also Sabatier, *Ber.*, 1885, 18, 493.

⁶ Smith and Brownlee, *Zeitsch. physikal. Chem.*, 1907, 61, 209; Brownlee, *J. Amer. Chem. Soc.*, 1907, 29, 1032.

⁷ Deville, *loc. cit.*; Domergue, *Ann. Chim. anal.*, 1904, 9, 445; Taurel and Griffet, *Compt. rend.*, 1911, 152, 1182; Noyer, *Caoutchouc et Gutta-percha*, 1918, 15, 9661.

⁸ Selmi, *loc. cit.*; Müller, *Ann. Phys. Chem.*, 1866, [ii.], 127, 404; Cross and Higgin, *Ber.*, 1883, 6, 1195.

⁹ Troost and Hautefeuille, *Compt. rend.*, 1869, 69, 48; Petersen, *Zeitsch. physikal. Chem.*, 1891, 8, 609.

¹⁰ Petersen, *loc. cit.*; Berthelot, *Compt. rend.*, 1870, 70, 941; Favre, *J. Pharm. Chim.*, 1863, [iii.], 24, 344; Favre and Silbermann, *Ann. Chim. Phys.*, 1852, [iii.], 34, 447.

¹¹ Threlfall, Brearley and Allen, *Proc. Roy. Soc.*, 1894, 56, 37; Judd, *Trans. Chem. Soc.*, 1890, 57, 404.

ing,¹ either alone or with alcohol or an animal or vegetable oil; if the γ -sulphur is heated until it becomes fluid, the phenomena observed will be those already described for liquid sulphur. The products from "plastic sulphur" and from sodium thiosulphate are amongst the least stable forms of γ -sulphur whilst those from the sulphur halides are relatively very stable. By treatment with an aqueous solution of a mineral acid such as sulphuric or sulphurous acid, the stability of the products may be increased.

That under suitable conditions γ -sulphur can retain its individuality for a considerable period is clearly demonstrated by the fact that "insoluble sulphur" has been found in a specimen of "flowers of sulphur" prepared more than fifty years previously. Indeed, the presence of "insoluble sulphur" serves as a trustworthy characteristic of genuine "flowers of sulphur" by which the fraudulent substitution of powdered sulphur may easily be detected.

When prepared by chemical methods, γ -sulphur is frequently accompanied by an apparently amorphous powder which is readily soluble in carbon disulphide. This has been regarded, by some investigators, as a definite form of sulphur and given the name "*soluble amorphous sulphur*";² in reality, however, it consists of minute spheroidal crystals of rhombic sulphur possibly together with nacreous sulphur.³ Another so-called modification of amorphous sulphur, described⁴ as soluble in carbon disulphide but becoming insoluble on evaporation of the solvent, is probably no distinct form, but only a mixture of γ -sulphur with finely divided crystalline sulphur.

It is probable that the inconstancy of the results obtained by various investigators for the specific gravity and other characteristics of γ -sulphur is due to contamination of the substance examined with other forms of sulphur or with foreign substances. Such a probability is increased by the description of a hydrated form of amorphous sulphur the composition of which points to its being a definite *hydrate*, $S_8 \cdot H_2O$; this compound is stated to be obtainable by the interaction of hydrogen sulphide and sulphurous acid in aqueous solution.⁵

"*Milk of Sulphur*" or "*Precipitated Sulphur*" of commerce, which is prepared by precipitating with acid a solution of calcium polysulphide (obtained by heating an aqueous emulsion of slaked lime with finely divided sulphur, see p. 67) or of "*liver of sulphur*" (obtained by fusing together potassium carbonate and sulphur), is also a mixture of finely divided rhombic sulphur with the insoluble amorphous γ -sulphur. It owes the paleness of its colour and its especial suitability for internal medicinal application to its very fine state of division.⁶ γ -Sulphur in reactivity is very little different from ordinary crystalline sulphur.⁷

¹ Smith and Holmes, *Zeitsch. physikal. Chem.*, 1903, 42, 489; Huerre, *J. Pharm. Chim.* 1923, [vii.], 28, 223; Magnus, *Ann. Phys. Chem.*, 1854, [ii.], 92, 308; Fordos and Gélis, *Ann. Chim. Phys.*, 1851, [iii.], 32, 385; Brodie, *Proc. Roy. Soc.*, 1854, 7, 24; Berthelot, *Compt. rend.*, 1857, 44, 318.

² Berthelot, *Ann. Chim. Phys.*, 1857, [iii.], 49, 430; 50, 376; *Compt. rend.*, 1870, 70, 941.

³ Petersen, *Zeitsch. physikal. Chem.*, 1891, 8, 608; Muthmann, *Zeitsch. Kryst. Min.*, 1890, 17, 342, 398.

⁴ See, e.g., Magnus, *Ann. Phys. Chem.*, 1856, [ii.], 99, 145; Weber, *ibid.*, 1870, [ii.], 141, 432.

⁵ Spring, *Rev. Trav. chim.*, 1906, 25, 253. See also Debus, *Chem. News*, 1888, 57, 87.

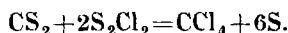
⁶ Sabbatini, *Biochem. Zeitsch.*, 1914, 59, 378.

⁷ Péan de St Gilles, *Ann. Chim. Phys.*, 1858, [ii.], 54, 49; *Compt. rend.*, 1858, 48, 398; Muller-Erzbach, *Annalen*, 1883, 18, 114; Schmitz-Dumont, *Ber.*, 1892, 25, 2659.

π-Sulphur, a deep yellow amorphous form of sulphur soluble in carbon disulphide, has already been described (p. 17).

Other forms of amorphous sulphur, which have been described at various times in chemical literature, are the so-called "*blue sulphur*" and "*black sulphur*"; our present state of knowledge of these is far from satisfactory, and their existence as definite modifications of pure sulphur is questionable, especially in the case of the latter variety, the colour of which appears to be due to small quantities of carbon or of metallic sulphides.¹

When a concentrated solution of ferric chloride is rapidly mixed with fifty to one hundred times its volume of aqueous hydrogen sulphide solution the liquid assumes a transient blue colour, sulphur subsequently precipitating in the ordinary yellowish-white form.² Sulphur with a blue coloration is also obtained in the interaction of carbon disulphide and sulphur chloride, for the preparation of carbon tetrachloride, under the catalytic influence of ferric chloride,



By submitting various metallic sulphides, *e.g.* those of bismuth, silver, cadmium or zinc, to the action of a solution of sulphur chloride in benzene or toluene, a greenish-blue precipitate of sulphur is obtainable, but the product invariably contains several units per cent. of mineral impurity.³ The suggestion that Ultramarine owes its colour to the presence of a blue variety of sulphur appears to have little probability, especially in view of the stability of this substance towards heat,⁴ and indeed the true nature of the blue- or green-coloured precipitates of sulphur, obtained by any of the afore-mentioned methods, requires much more experimental investigation before the existence of a blue or green modification of sulphur can be accepted.

Sulphur, however, dissolves in certain organic liquids, for example, hot glycerol or ethylene glycol, and in pyrosulphuric acid, yielding clear blue solutions.⁵ Cryoscopic measurements with solutions in the latter solvent indicate that the sulphur molecules are diatomic, and it is to be assumed that this is also the case with the blue solutions in organic solvents. Thus, in such solutions the sulphur is more highly dispersed than in most organic solvents, in which the molecules are octatomic.

The existence of a black form of sulphur was first suggested by Mitscherlich in 1856, who observed that in the presence of very slight traces of organic impurities, plastic sulphur could be obtained with a very deep or even black colour;⁶ the necessity for the presence of

¹ Neumann, *Zeitsch. angew. Chem.*, 1917, 30, 1, 165.

² Wöhler, *Annalen*, 1853, 86, 373; Vogel, *J. Pharm. Chem.*, 1856, [iii.], 29, 433. See also Schiff, *Annalen*, 1860, 115, 68.

³ Orloff, *J. Russ. Phys. Chem. Soc.*, 1901, 33, 397; 1902, 34, 52. See also Stook and Blux, *Ber.*, 1901, 34, 3039; Erdmann, *Annalen*, 1908, 362, 133; von Weimarn, *J. Russ. Phys. Chem. Soc.*, 1915, 47, 2177; Guareschi, *Atti R. Accad. Sci. Torino*, 1916, 51, 951; Rohland, *Kolloid-Zeitsch.*, 1915, 16, 145; Ruff and Geisel, *Ber.*, 1905, 38, 2659.

⁴ Paternò and Mazzucchelli, *Atti R. Accad. Lincei*, 1907, [v.], 16, i., 465; Puchner, *Kolloid-Zeitsch.*, 1915, 16, 145; Hoffmann, *Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 275.

⁵ von Weimarn, *J. Russ. Phys. Chem. Soc.*, 1915, 47, 2177; *Koll. Chem. Beihefte*, 1926, 22, 38; Ostwald and Auerbach, *Kolloid-Zeitsch.*, 1926, 38, 336; Auerbach, *Zeitsch. physikal. Chem.*, 1926, 121, 337.

⁶ Mitscherlich, *J. prakt. Chem.*, 1856, 67, 369; Moutier and Dietzenbacher, *Compt. rend.*, 1865, 60, 353; Dietzenbacher, *Ann. Phys. Chem.*, 1865, [ii.], 124, 644; Magnus,

foreign matter, however, greatly discredits any claim of this variety to be a distinct allotropic form.

Sulphur thus presents a most remarkable example of polymorphism. Indeed, on account of the complexity of its behaviour in this direction, much further investigation will be required before any attempt at a full and general interpretation of the phenomena will be possible.

COLLOIDAL SULPHUR.

Colloidal sulphur, sometimes designated δ -sulphur, consists of sulphur in such small particles that these can remain suspended in water as a "colloidal solution." Such a suspension is readily formed by rapidly pouring an alcohol solution of sulphur into water,¹ or similarly treating a solution of sulphur in hydrazine hydrate.² Cathodic pulverisation, as applied commonly to the production of colloidal solutions of metallic substances, has also been successfully extended to sulphur.³

When hydrogen sulphide is passed into a solution of sulphurous acid (see p. 128) some of the sulphur remains in colloidal solution, the amount and degree of dispersion depending on the concentration of the sulphur dioxide,⁴ both increasing to a maximum as the latter decreases and then falling rapidly; the degree of dispersion of the sulphur thus decreases with its concentration. The formation of sulphur sol by the action of hydrochloric or sulphuric acid on aqueous solutions of sodium thiosulphate decreases with increasing concentration of the reactants and also decreases somewhat with lowering of temperature. After the formation of sulphur sol by these chemical methods, the mixture should immediately be flocculated by the addition of pure sodium chloride and the precipitate separated by centrifuging the liquid. The sulphur obtained is largely redispersible in water, forming a hydrosol, any undispersed portion being removable by sedimentation.⁵

On account of the tendency of the suspended particles to coalesce, colloidal solutions of sulphur are generally short-lived. The stability of the solutions can be increased by the addition of a "protective colloid" such as albumen or gelatine. The action of hydrochloric acid on sodium thiosulphate solution yields a colloidal solution which is more stable if the reagents are used in a concentrated condition,⁶ but the life of the unstable colloidal solution obtained with dilute reagents can be extended by the addition of gelatine. Also, by preparing the sulphur in a wet way in the presence of albumen, the

¹ *ibid.*, 1854, [ii.], 92, 308; Keller, *Bull. Soc. chim.*, 1865, [ii.], 4, 346; Knapp, *J. prakt. Chem.*, 1888, [ii.], 38, 48; Ber., 1891, 24, 615. See also Jones, *Chem. News*, 1880, 41, 244.

² von Weimarn and Maljischeff, *J. Russ. Phys. Chem. Soc.*, 1910, 42, 484.

³ Meyer, *Ber.*, 1913, 46, 3089; Ostwald and Egger, *Kolloid-Zeitsch.*, 1927, 43, 353.

⁴ Müller and Nowakowski, *Ber.*, 1905, 38, 3778.

⁵ Odén, *Nova acta, Upsala*, 1913, [iv.], 3, No. 4, 1.

⁶ Cf. Raffo, *Zeitsch. Chem. Ind. Kolloide*, 1908, 2, 358.

⁷ Lobry de Bruyn, *Rec. Trav. chim.*, 1900, 19, 236. See also Raffo and others, *Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 158; 1911, 9, 58; 1912, 10, 278; 11, 121; *Kolloid-Zeitsch.*, 1912, 13, 289; *Gazzetta*, 1913, 45, i., 119; also Garard and Colt, *J. Amer. Chem. Soc.*, 1927, 49, 630; Lora and Tamayo, *Anal. Fis. Quím. (Tecn.)*, 1929, 27, 110. For the influence of mercaptan, see Iwase, *Kolloid-Zeitsch.*, 1928, 45, 31.

precipitate can subsequently be washed, dispersed in water containing a trace of alkali, and the sulphur obtained finally as a greyish-white amorphous substance by dialysis and evaporation of the colloidal solution; the product contains 95 per cent. of sulphur and on dispersion in water gives an opalescent sol.¹

Sulphur sols may also be prepared by intensively grinding together pure sulphur and grape sugar in an agate mortar and treating with water.²

Highly dispersed sols, containing up to 0.082 per cent. of sulphur, may be obtained³ by passing superheated sulphur vapour, free from air, into air-free water. The sols have an acid reaction due to traces of polythionic acids and hydrogen sulphide. They are white and remain stable for several weeks.

Sulphur sols generally are opalescent, with a yellowish-white to yellow colour; when viewed by transmitted light they commonly appear bluish, but if freshly formed may exhibit successively the colours yellow, green, red, violet and blue. Such colour changes, which depend upon the degree of dispersion of the sulphur, may conveniently be shown⁴ by adding a dilute solution of phosphoric acid to *N*/25 sodium thiosulphate solution. The yellow or brown colour produced by sulphur in sodium-calcium silicate glass⁵ is not due to colloidal sulphur, but is probably caused by the formation of polysulphides.⁶

Colloidal sulphur is usually hydrophilic and capable of absorbing water to a considerable degree. The absorption is favoured by the presence in solution of small amounts of acid or salts of univalent metals, but salts of bivalent metals hinder the absorption and cause precipitation.⁷ Sols prepared by von Weimarn's method, *i.e.* by pouring an alcohol solution of sulphur into water, are, however, completely hydrophobic.⁸ They are negatively charged and are readily coagulated by electrolytes; alkali salts have a ten to twenty times stronger coagulating action on them than on sols prepared by the interaction of hydrogen sulphide and sulphurous acid, or the decomposition of thionic acids. It is evident that the micelles in the two types of sols are not identical; the sulphur is in a highly polymerised condition and the hydrophilic colloid appears to contain pentathionic acid; this acid can be detected in the filtrate after coagulation. Moreover, hydrophilic sols are produced by reactions which yield both sulphur and pentathionic acid, as in the decomposition of sulphur monochloride by water:



A sulphur sol containing sulphuric acid and sodium sulphate, which act as stabilisers, has an electrical conductivity lower than that of a similar solution containing no colloidal sulphur; the freezing-point is

¹ Chemische Fabrik von Heyden, *German Patent*, 164664 (1905); *J. Soc. Chem. Ind.*, 1906, 25, 284; Himmelbauer, *Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 307.

² von Weimarn and Utzino, *Mem. Coll. Sci. Kyōto*, 1925, A, 8, 291.

³ Gutbier, *Zeitsch. anorg. Chem.*, 1926, 152, 163. See also Winkler and Giller, *German Patent*, 431505 (1925); Dittler, *Kolloid-Zeitsch.*, 1917, 21, 27.

⁴ Auerbach, *Kolloid-Zeitsch.*, 1920, 27, 223. See also p. 29.

⁵ Ebell, *Ber.*, 1878, 11, 1136; Selezner, *ibid.*, 1882, 15, 1191.

⁶ Fenaroli, *Kolloid-Zeitsch.*, 1915, 16, 53.

⁷ Barry, *Compt. rend.*, 1920, 171, 433; von Weimarn and Utzino, *Kolloid-Zeitsch.*, 1926, 26, 265.

⁸ Freundlich and Scholtz, *Koll. Chem. Beihefte*, 1922, 16, 234.

also higher.¹ If such a colloidal sulphur solution is dialysed, and then to the dialysed solution sulphuric acid and sodium sulphate are added in the amounts originally present, the electrical conductivity of the resulting solution will have the same higher value as a similar solution from which the sol has been removed. It must be assumed therefore that when the sol is first formed the sulphur reacts in some way with the electrolytes, probably causing a change in their physical nature, this resulting in a reduction in electrical conductivity and osmotic pressure. Further quantities of the electrolytes added after the formation of the colloid are not affected by the colloid.

The transformation of maleic acid to fumaric acid is accelerated by the presence of colloidal sulphur.²

GENERAL PHYSICAL PROPERTIES OF SULPHUR.

Solid sulphur does not conduct electricity appreciably³ and so forms a convenient insulating material for some purposes, although it is more frequently used only as an ingredient of insulating compounds or mixtures. When rubbed, sulphur becomes negatively charged, although on exposure to radium radiation it becomes charged positively.⁴ Molten sulphur conducts electricity appreciably, although impurities may contribute in part to this characteristic behaviour.⁵ The conductivity of the liquid⁶ increases to a maximum at about 160° C., falls to a minimum at about 185° C., and thereafter increases (cf. viscosity changes, p. 16). The specific resistance at 163° C. is approximately 7.5×10^{10} ohms.⁷ The dielectric constant of solid sulphur is approximately 2.7,⁸ although variation occurs according to the axis along which the measurement is made. For the liquid, supercooled between 150° and 95° C., the Clausius-Mossotti law is followed.⁹ Sulphur is diamagnetic.¹⁰

¹ Rossi, *Kolloid-Zeitsch.*, 1922, 30, 228; 1924, 34, 20; *Gazzetta*, 1924, 54, 65; *Zymologica*, 1927, 2, 63; Raffo and Rossi, *Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 121; *Gazzetta*, 1912, 42, [ii.], 326.

² Skraup, *Monatsh.*, 1891, 18, 107; Freundlich and Schikorr, *Koll. Chem. Beihefte*, 1926, 22, 1. For further observations on colloidal sulphur, see Svedberg, *Zeitsch. Chem. Ind. Kolloide*, 1909, 4, 49; Liesegang, *ibid.*, 1910, 7, 307; Lifschitz and Brandt, *Kolloid-Zeitsch.*, 1918, 22, 133; Browne, *Colloid Symposium Monograph*, Univ. Wisconsin, 1923, p. 7; Johlin, *J. Physical Chem.*, 1925, 29, 1129; Pokrowski, *Zeitsch. Physik*, 1926, 37, 172; 40, 368; Fodor and Rivlin, *Kolloid-Zeitsch.*, 1928, 44, 69; Ghosh and Dhar, *ibid.*, p. 218; Messini, *Arch. exp. Path. Pharm.*, 1928, 127, 366.

³ Threlfall, Brearley and Allen, *Proc. Roy. Soc.*, 1894, 56, 32; Duter, *Compt. rend.*, 1888, 106, 836; Monckman, *Proc. Roy. Soc.*, 1889, 46, 136; Guerasimov, *J. Russ. Phys. Chem. Soc.*, 1926, 58, 201.

⁴ Hoeschus and Georgiewski, *J. Russ. Phys. Chem. Soc.*, 1905, 37, 29. The photoelectric conductivity of sulphur has been investigated by Kurrelmeyer, *Phys. Review*, 1927, ii., 30, 893.

⁵ Bidwell, *Phil. Mag.*, 1885, [v.], 20, 178; *Ber.*, 1885, 18, 696.

⁶ Black, *Proc. Camb. Phil. Soc.*, 1924, 22, 393; cf. Wigand, *Ber. deut. physikal. Ges.*, 1908, 6, 495.

⁷ For measurements obtained in a vacuum, see Neumann, *Zeitsch. Physik*, 1927, 45, 717.

⁸ Lefebvre, *Compt. rend.*, 1891, 113, 660; Thwing, *Zeitsch. physikal. Chem.*, 1894, 14, 286; Threlfall, Brearley and Allen, *loc. cit.*; Threlfall and Brearley, *Phil. Trans.*, 1896, A, 187, 57; Boltzmann, *Wien. Akad. Ber.*, 1874, 70, 342; Gordon, *Proc. Roy. Soc.*, 1879, 28, 155; Thomson, *ibid.*, 1889, 46, 292.

⁹ Rosental, *Bull. Acad. Polonaise*, 1928, A, 1, 377.

¹⁰ Carnelley, *Chem. News*, 1879, 40, 183.

On account of its low heat conductivity solid sulphur breaks readily when warmed, the uneven expansion caused by the warmth of the hand being sufficient to cause an audible sound of cracking.¹ The following values for the thermal conductivity of sulphur over the temperature range 20° to 210° C. have been obtained: ²

Form.	Temperature, ° C.	Thermal Conductivity.
Rhombic	20	0.00065
"	40	0.00061
"	60	0.00058
"	80	0.00055
"	95 { transition point	0.00054
Monoclinic	100	0.00037 to 0.00040
Plastic	20	0.0002
Liquid	115 (m.pt.)	0.00031
"	120	0.00031
"	140	0.00032
"	160 { transition point	0.00033
"	165 { point	0.00033
"	170 { region	0.00034
"	190	0.00036
"	210	0.00037

The latent heat of fusion of solid sulphur varies with the different allotropic forms and with the temperature; it is lowest for octahedral sulphur; it is also influenced by the proportion of insoluble sulphur (γ - or μ -) in the original solid and in the liquid formed.³ By electrical heating at the melting-point, the latent heat of fusion of monoclinic sulphur has been found to be ⁴ 8.85 gm.-cals. per gm.

The latent heat of evaporation of sulphur (within an estimated accuracy of 2 per cent.) is 79.⁵

As has already been mentioned, the behaviour of molten sulphur on crystallisation is of a complex nature and dependent largely on the previous temperatures, the rate of cooling and the temperature at which crystallisation begins.⁶ Occasionally crystallisation occurs in a rhythmic manner, giving rise to an annular appearance in the structure of the solid mass.⁷ The crystallisation of undercooled molten sulphur is stated

¹ Daguin, *Compt. rend.*, 1845, 20, 1667.

² Kaye and Higgins, *Proc. Roy. Soc.*, 1929, [A], 122, 633.

³ Lewis and Randall, *J. Amer. Chem. Soc.*, 1911, 33, 476; 1914, 36, 2468; Wigand, *Zeitsch. physikal. Chem.*, 1908, 63, 273. For the heat of vaporisation, see Traube, *Ber.*, 1898, 31, 1562.

⁴ Stratton and Partington, *Phil. Mag.*, 1922, 43, 442; cf. Wigand, *loc. cit.*

⁵ Awbery, *Proc. Physical Soc.*, 1927, 39, 417.

⁶ Gernez, *Compt. rend.*, 1876, 82, 1153; 1883, 97, 1298; Duhem, *Zeitsch. physikal. Chem.*, 1897, 23, 254; Tammann, *ibid.*, 1897, 23, 326; Gaubert, *Compt. rend.*, 1916, 162, 554.

⁷ Fischer-Treuenfeld, *Kolloid-Zeitsch.*, 1915, 16, 109; Köhler, *Kolloid-Zeitsch.*, 1915, 17, 10.

to be accelerated by the action of radium radiation, probably by the β -rays.¹

In the molten condition the density of sulphur is dependent only on the temperature, provided that the equilibrium condition between λ -sulphur and μ -sulphur has been attained; at 118° C. the density is 1.811, the value then rising somewhat up to about 160° C.,² then steadily falling to 1.480 at 446° C. The coefficient of expansion has been measured by several investigators,³ but on account of the complications introduced by the gradual readjustment of the equilibrium at new temperatures, the results are not altogether concordant, although they supply confirmatory evidence of the existence of the equilibrium. The mean specific heat of mobile sulphur is 0.220 and of viscous sulphur 0.290.⁴

The remarkable variations in the viscosity of molten sulphur have already been mentioned. Definite measurements have been made at a series of temperatures by the method of rotating cylinders,⁵ and it has been found that exposure of the liquid to air, especially below 160° C., has a marked effect on the viscosity from 160° C. onwards. The viscosity of purified (twice distilled but not gas-free) sulphur has a value at 123° C. of 0.1094 C.G.S. units; this falls to a minimum of 0.0709 at 150° C., rises gradually up to about 159° C., then rapidly increases above this temperature; an exact transition point is not observed, however. The maximum for purified unexposed (gas-free) sulphur occurs at about 200° C. and has a value of 215 C.G.S. units. For purified (not gas-free) sulphur after prolonged exposure to the air, the maximum occurs at about 190° C. and may have a value as high as 800 C.G.S. units. Such high viscosity appears to be due to impurities, the chief being sulphuric acid, resulting from exposure to the air; sulphur dioxide and ammonia in solution also have an appreciable effect.

The surface tension of liquid sulphur has been determined for different temperatures by several workers, whose results, however, are not in harmony.⁶ Kellas,⁷ in disagreement with the data of earlier workers, maintains that the surface tension of sulphur falls continuously from the melting-point to the boiling-point, and gives the following values:

119.4° C.	60.46 dynes per cm.
156 ° C.	56.38 „ „
280 ° C.	48.2 „ „
445 ° C.	39.4 „ „

Although sulphur exerts an appreciable vapour pressure at the ordinary and slightly elevated temperatures,⁸ the boiling-point is not

¹ Frischauer, *Compt. rend.*, 1909, 140, 1251.

² Ramsay, *Trans. Chem. Soc.*, 1879, 35, 463; Drugman and Ramsay, *J. Amer. Chem. Soc.*, 1895, 17, 1228; Arons, *Ann. Phys. Chem.*, 1894, [iii.], 53, 106; Mondain-Monval and Schneider, *Compt. rend.*, 1928, 186, 1356.

³ Toepler, *Ann. Phys. Chem.*, 1892, [iii.], 47, 169; Scichlone, *Gazzetta*, 1877, 7, 501; Despretz, *Compt. rend.*, 1838, 7, 590; Kopp, *Annalen*, 1855, 93, 129; Pisati, *Gazzetta*, 1874, 4, 29; 1877, 7, 337; Deville and Troost, *Ber.*, 1880, 13, 2019.

⁴ Mondain-Monval, *Compt. rend.*, 1926, 182, 58.

⁵ Farr and Macleod, *Proc. Roy. Soc.*, 1920, [A], 97, 80.

⁶ Pisati, *Gazzetta*, 1877, 7, 357; Zickendraht, *Ann. Physik*, 1906, [iv.], 21, 141; Capelle, *Bull. Soc. chim.*, 1908, [iv.], 3, 764; Rudge, *Proc. Camb. Phil. Soc.*, 1910, 16, 55.

⁷ Kellas, *Trans. Chem. Soc.*, 1918, 113, 903.

⁸ Krafft and Merz, *Ber.*, 1903, 36, 4344; Jones, *Mem. Manchester Phil. Soc.*, 1912, 56,

reached until 444.60°C . (at 760 mm.).¹ This temperature is a definite constant² and enables sulphur to be used as a solvent for the ebullioscopic determination of molecular weights,³ the following "molecular formulæ" having been determined experimentally for the respective elements dissolved in sulphur: $\text{Se}_{2.4}$, $\text{Te}_{1.3}$, $\text{As}_{1.0}$, and $\text{Sb}_{1.2}$. The boiling-point (t) at various pressures may be obtained from the equation:⁴

$$t = 444.60 + 0.0910(p - 760) - 0.000049(p - 760)^2.$$

The refractive index of liquid sulphur has been investigated and is found to decrease up to 160°C . and then increase above that temperature.⁵

With regard to the spectrum of sulphur, the most persistent lines in the emission spectra are of the following wave-lengths (\AA):⁶

1807.4	4694.2	9212.8
1820.5	4695.5	9228.2
1826.4	4696.3	9237.7.

On vaporising sulphur in a cooled hydrogen flame, or on passing feeble electric sparks through the vapour contained in a Geissler tube, a band spectrum is obtained consisting of a series of bands sharp on the

[14], 1, Moss, *Sci. Proc. Roy. Dublin Soc.*, 1906, **11**, 105; Cross and Higgin, *Ber.*, 1883, 6, 1195; Brame, *Ann. Phys. Chem. Beibl.*, 1881, [iii.], 5, 856; Berthelot, *Compt. rend.*, 1885, 100, 1326; Dewar, *Proc. Roy. Soc.*, 1865, **14**, 7; Porter, *Proc. Chem. Soc.*, 1898, **14**, 65; Gruener, *J. Amer. Chem. Soc.*, 1907, **29**, 1396; Ruff and Graf, *Zeitsch. anorg. Chem.*, 1908, **58**, 209; *Ber.*, 1907, **40**, 4199; Chavastelon, *Compt. rend.*, 1923, **177**, 1040, 1217. For the measurement of the vapour pressure at different temperatures, see the last two references; also Matthies, *Physikal. Zeitsch.*, 1906, **7**, 397; Mueller and Burgess, *J. Amer. Chem. Soc.*, 1919, **41**, 745. For an investigation of the rate of sublimation of sulphur between 25° and 50°C , see Tucker, *Ind. Eng. Chem.*, 1929, **21**, 44.

¹ Chappuis, *Bur. Int. Poids Mes.*, 1917, Mem. 16; Eumorfopoulos, *Proc. Roy. Soc.*, 1908, [A], **81**, 339; 1914, [A], **90**, 189; Callendar, *ibid.*, 1908, [A], **81**, 363; Callendar and Moss, *ibid.*, 1909, [A], **83**, 106; Callendar and Griffiths, *ibid.*, 1891, **49**, 56; Day and Sosman, *J. Washington Acad. Sci.*, 1912, **2**, 167; Ramsay, *Trans. Chem. Soc.*, 1879, **35**, 463; Carnolley and Williams, *ibid.*, 1878, **33**, 281; Hittorf, *Ann. Phys. Chem.*, 1865, [u.], **126**, 196.

² Meissner, *Ann. Physik*, 1912, [iv.], **39**, 1230.

³ Beckmann and Liesche, *Zeitsch. anorg. Chem.*, 1914, **85**, 31.

⁴ Mueller and Burgess, *loc. cit.*

⁵ Mondain-Monval and Schneider, *Compt. rend.*, 1928, **186**, 1356. For refractive index and dispersion of sulphur vapour, see Cuthbertson and Metcalfe, *Proc. Roy. Soc.*, 1908, [A], **80**, 411. For the refractivity of sulphur in organic compounds, see Price and Twiss, *Trans. Chem. Soc.*, 1912, **101**, 1259; Delépine, *Ann. Chim. Phys.*, 1912, [viii], **25**, 529.

⁶ *International Critical Tables*, National Research Council, U.S.A., 1929, v., 324. See Plucker and Hittorf, *Proc. Roy. Soc.*, 1864, **13**, 153; *Phil. Mag.*, 1864, [iv.], **28**, 64; Seguin, *Compt. rend.*, 1861, **53**, 127; Salet, *ibid.*, 1869, **68**, 404; 1871, **73**, 559; Hartley, *Phil. Trans.*, 1893, **105**, 161; de Gramont, *Compt. rend.*, 1894, **119**, 68; Evershed, *Phil. Mag.*, 1895, [v.], **39**, 460; Runge and Paschen, *Ann. Chem. Phys.*, 1897, [iii.], **61**, 669; Rancken, *Zeitsch. anorg. Chem.*, 1898, **18**, 86; Eder and Valenta, *Sitzungsber. K. Akad. Wiss. Wien*, 1898, **67**, 97; Exner and Haschek, *Die Spektren der Elemente bei normalen Druck*, Wien, 1912, vol. 3; Meissner, *Physikal. Zeitsch.*, 1914, **15**, 668; Stark and Künzer, *Ann. Physik*, 1914, [iv.], **45**, 29; Bowen and Millikan, *Phys. Review*, 1925, **25**, 295, 591, 600; 26, 150; Bungartz, *Ann. Physik*, 1925, [iv.], **76**, 709; Bhattacharyya, *Proc. Roy. Soc.*, 1929, [A], **122**, 416; *Nature*, 1928, **122**, 241. For higher order spectra, S II., see Bloch and Bloch, *Compt. rend.*, 1927, **185**, 761; 1929, **188**, 160; Gilles, *ibid.*, 1928, **186**, 1109, 1354; Lacroute, *ibid.*, 1928, **187**, 975; *J. Phys. Radium*, 1928, [vi.], **9**, 180; Ingram, *Phys. Review*, 1928, [i.], **32**, 172. S III., see Gilles, *Compt. rend.*, 1929, **188**, 63, 320. S IV., see Bowen, *Phys. Review*, 1928, [ii.], **31**, 34. For the influence of argon on the spectrum of sulphur, see Johnson and Cameron, *Proc. Roy. Soc.*, 1924, [A], **106**, 195; McLennan, Ruedy and Howlett, *Trans. Roy. Soc. Canada*, 1928, [iii.], **22**, III., 79.

violet side but shading off towards the red and extending right across the visible region.¹

The changes in the absorption spectrum of sulphur vapour over the range 400° to 1200° C. have already been mentioned (p. 15). In the ultra-violet region the spectrum has been investigated² over the range 100° to 1000° C. under low pressures (0.5 to 53 mm.) using a continuous spark under water as a background. Below 250° C. continuous absorption occurs between 2700 and 2800 Å, but at higher temperatures, as S₂ molecules appear, and under 0.5 mm. pressure, a band spectrum between 2927 and 2713 Å appears, which, with rise in temperature, continues to extend until it covers the region 3700 to 2475 Å. It is then composed of three distinct sets of bands, viz. :

- (i) 3700 to 2794 Å, bands of fine structure ;
- (ii) 2794 „ 2592 Å, narrow bands without fine structure ;
- (iii) 2592 „ 2475 Å, broad continuous bands.

There is a band of maximum absorption³ at 2750 Å.

The fluorescence spectrum⁴ of sulphur vapour under excitation by light from a mercury arc gives a series of bands extending over the visible region.

The absorption of light by thin layers of sulphur (0.3 mm.) at 0° C.⁵ is continuous from the ultra-violet to 4080 Å, and extends a further 20 Å towards the red for every 10° rise in temperature up to 300° C., no discontinuity, such as might be expected (see p. 15), being observed in the neighbourhood of 160° C.

The absorption of ultra-violet light by colloidal solutions of sulphur has been examined,⁶ and is found to vary with the size of the colloid particle, approaching a limit corresponding with the amount absorbed by a molecular solution of sulphur in alcohol.

CHEMICAL PROPERTIES OF SULPHUR.

Sulphur is less electronegative than oxygen and the halogens. It combines directly with most of the elements, notable exceptions being nitrogen, gold, platinum and beryllium.

When heated in oxygen or in air it inflames near 260° C.⁷ with

¹ Salet, *Ann. Chim. Phys.*, 1873, [iv.], 28, 37 ; *Compt. rend.*, 1869, 68, 404 ; Gernez, *ibid.*, 1872, 74, 804 ; Nichols and Snow, *Phil. Mag.*, 1891, [v.], 32, 401 ; de Gramont, *Compt. rend.*, 1896, 122, 1326.

² Henri and Treves, *ibid.*, 1924, 179, 1156 ; *Nature*, 1924, 114, 894. See also Sharer, *Trans. Roy. Soc. Canada*, 1924, [iii.], 18, III., 145 ; Rosen, *Zeitsch. Physik*, 1927, 43, 69 ; 1928, 48, 545 ; Gilles, *Compt. rend.*, 1929, 188, 1607. The X-ray spectra have been investigated by Lindh, *Compt. rend.*, 1922, 175, 25 ; Hopfield and Birge, *Nature*, 1923, 112, 437, 790 ; Hopfield, *Phys. Review*, 1925, [ii.], 26, 282 ; Bowen and Millikan, *ibid.*, 1925, [ii.], 25, 59, 295, 600 ; Ray, *Phil. Mag.*, 1925, [vi.], 50, 506 ; Robinson, *Nature*, 1925, 115, 945 ; Allison, *J. Washington Acad. Sci.*, 1926, 16, 7. For spectral frequencies in the region between light- and X-rays, see Holweck, *Compt. rend.*, 1925, 180, 266, 658 ; *J. Chim. phys.*, 1925, 22, 311.

³ Norrish and Rideal, *Trans. Chem. Soc.*, 1924, 125, 2070 ; Graham, *Proc. Roy. Soc.*, 1910, [A], 84, 311.

⁴ McLennan and Walcrstein, *Phys. Review*, 1927, [ii.], 29, 208 ; with Grayson Smith, *Phil. Mag.*, 1927, [vii.], 3, 390 ; Rosen, *Zeitsch. Physik*, 1927, 43, 69.

⁵ Fukuda, *Mem. Coll. Sci. Kyōto*, 1921, 4, 351.

⁶ Pihlblad, *Zeitsch. physikal. Chem.*, 1917, 92, 471.

⁷ Blount, *Chem. News*, 1890, 61, 108, 153 ; Hill, *ibid.*, 1890, 61, 125 ; *Pharm. J.*, 1907, [iv.], 24, 288 ; Moissan, *Compt. rend.*, 1903, 137, 547 ; McCrea and Wilson, *Chem. News*, 1907, 96, 25.

formation of sulphur dioxide and a little sulphur trioxide (see p. 108). As would be expected, the atomic heat of combustion¹ of octahedral sulphur (71,080 calories per gram-atom) is less than that of prismatic sulphur (71,720 calories) if considered at the ordinary temperature, the difference being equal to the heat of transformation of the one form into the other. According to Mondain-Monval,² however, the transition $S_\alpha \rightarrow S_\beta$ absorbs only 87 calories per gram-atom.

At 200° C. sulphur can undergo slow oxidation,³ manifested by a distinct phosphorescence;⁴ oxidation can also occur even at the ordinary temperature,⁵ especially with finely divided sulphur in a moist condition. "Flowers of sulphur," when stirred with water, usually imparts a feeble acid reaction to the liquid. To this slow oxidation probably is to be attributed any beneficial effects resulting from the customary introduction of lumps of sulphur into dogs' drinking troughs (cf. p. 12).

Sulphur is soluble in solutions of the sulphides of the alkali metals, including ammonium, with the formation of yellow solutions of polysulphides.⁶ The alkali carbonates and the hydroxides of the alkali and alkaline earth metals, in aqueous solution, also dissolve sulphur, producing sulphides or polysulphides together with thiosulphates and sulphites. In all probability the ideal equation for hydroxides is :



The main polysulphide products are trisulphide, tetrasulphide and pentasulphide, but on account of the tendency of the polysulphides to decompose, yielding thiosulphate and hydrogen sulphide, the quantity of thiosulphate usually exceeds that indicated in the equation.⁷ Loss of sulphur by the thiosulphate yields sulphite.⁸ The so-called "lime-sulphur" washes, used as insecticides in agricultural work, are obtained by treating sulphur with milk of lime in this way.⁹

Many metals combine readily with sulphur; for example copper in the form of foil or wire and the vapour of boiling sulphur react so vigorously, forming cuprous sulphide, that the metal becomes white-hot;¹⁰ sodium burns brilliantly on molten sulphur. The reaction

¹ Thomsen, *Ber.*, 1880, 13, 959; Petersen, *Zeitsch. physikal. Chem.*, 1891, 8, 609.

² Mondain-Monval, *Compt. rend.*, 1926, 182, 58.

³ Bodenstein and Karo, *Zeitsch. physikal. Chem.*, 1910, 75, 30.

⁴ Mulder, *J. prakt. Chem.*, 1863, 91, 112; Joubert, *Compt. rend.*, 1874, 78, 1853; Heumann, *Ber.*, 1883, 16, 139; Schwarz, *Zeitsch. anal. Chem.*, 1883, 22, 531; Jacobsen, *Ber.*, 1883, 16, 478; Bloch, *Compt. rend.*, 1909, 148, 782; Watson, *Chem. News*, 1913, 108, 187; Emeléus, *J. Chem. Soc.*, 1928, p. 1942.

⁵ Moissan, *loc. cit.*; Maly, *Monatsh.*, 1880, 1, 205; Pollacci, *Gazzetta*, 1874, 4, 177, 245, 469; *Boll. chim. farm.*, 1908, 47, 363; Brugnatelli and Pelloggio, *Ber.*, 1874, 7, 1462; 1875, 8, 71; Brioux and Guerbet, *Compt. rend.*, 1913, 156, 1476.

⁶ Küster and Heberlein, *Zeitsch. anorg. Chem.*, 1905, 43, 53.

⁷ Fahlberg and Iles, *Ber.*, 1878, 11, 1187; Fordos and Gélis, *Ann. Chim. Phys.*, 1846, [iii.], 18, 86; Senderens, *Bull. Soc. chim.*, 1891, [iii.], 6, 800; *Compt. rend.*, 1883, 96, 839; Tartar, *J. Amer. Chem. Soc.*, 1913, 35, 1746; 1914, 36, 495; Auld, *Trans. Chem. Soc.*, 1915, 107, 480; Thatcher, *J. Amer. Chem. Soc.*, 1908, 60, 63; Haywood, *ibid.*, 1905, 28, 244; Guareschi, *Compt. rend.*, 1916, 163, 390; Chapin, *J. Ind. Eng. Chem.*, 1916, 8, 339; Tartar and Draves, *J. Amer. Chem. Soc.*, 1924, 46, 574.

⁸ Calcagni, *Gazzetta*, 1920, 50, ii., 331.

⁹ Bodnar, *Chem. Zeit.*, 1915, 39, 715; Chapin, *J. Ind. Eng. Chem.*, 1916, 8, 339.

¹⁰ See Fieser, *Zeitsch. anorg. Chem.*, 1926, 154, 261. For the relation between velocity of reaction and composition of iron-sulphur mixtures, see Jarissen and Groenewald, *Rec. Trav. chim.*, 1928, 47, 737.

between aluminium and sulphur, started by means of magnesium and barium peroxide, takes place with explosive violence; also, magnesium and sulphur combine explosively if ignited by means of a mixture of sulphur and potassium chlorate.¹ Many investigations have been made on the fusion curves of mixtures of metals with varying amounts of sulphur, and the formation of compounds has been revealed in many cases;² antimony and sulphur under these conditions yield only Sb_2S_3 ,³ whilst lead and sulphur form only PbS .⁴

Most oxidising agents affect sulphur, the vigour of the action varying with the conditions and with the nature of the agent. A mixture of sulphur and potassium chlorate is highly explosive and will detonate violently on slight shock. Nitric acid oxidises sulphur quantitatively to sulphuric acid. When heated with sulphur, most metallic oxides are converted into sulphide and sulphate; mercury, lead, bismuth and cadmium oxides are common examples:⁵



In some cases, such as with the oxides of silver and copper, the sulphate can undergo further reduction by sulphur with formation of sulphide and sulphur dioxide; the oxides of zinc, tin and iron are not greatly attacked by sulphur, whilst chromium trioxide reacts so violently as to cause inflammation of the sulphur.⁶

Sulphates of the alkali and alkaline earth metals, when heated with sulphur, are converted into sulphide, polysulphide and thiosulphate, with simultaneous formation of sulphur dioxide; many other sulphates, e.g. those of copper, mercury, silver and lead, yield only sulphide.⁷ Other salts of the metals behave in a similar manner, undergoing transformation into sulphides, the change being effected more readily with the salts of the heavy metals, many of which indeed react slowly with sulphur even at 100°C . in the presence of water.⁸ At 150° to 200°C . mercuric, stannic and ferric salts in aqueous solution are quantitatively reduced by sulphur; mercurous, cupric, bismuth and lead salts are slowly but quantitatively precipitated as sulphides. Nitrates, permanganates and iodates cause oxidation of the sulphur to sulphuric acid.

With sufficiently powerful reducing agents, especially hydriodic acid, sulphur is reducible to hydrogen sulphide, and at higher temperatures a similar reduction can be effected by organic matter generally.⁹

Liquid ammonia dissolves sulphur with formation of an additive compound, $\text{S}(\text{NH}_3)_x$,¹⁰ decomposition slowly occurring with subsequent

¹ Danneel and Frohlich, *Zeitsch. angew. Chem.*, 1927, 40, 809.

² Pélabon, *Ann. Chim. Phys.*, 1909, [viii.], 17, 526; see also Schutz, *Metallurgie*, 1907, 4, 659, 694.

³ Jaeger and Klooster, *Zeitsch. anorg. Chem.*, 1912, 78, 245.

⁴ Friedrich and Leroux, *Metallurgie*, 1905, 2, 536. For the affinity of metals for sulphur, see Jellinek and Zakowski, *Zeitsch. anorg. Chem.*, 1925, 142, 1.

⁵ Senderens, *Bull. Soc. chim.*, 1891, [iii.], 6, 800.

⁶ Brückner, *Monatsh.*, 1906, 27, 199; Lassaigne, *Ann. Chim. Phys.*, 1820, [ii.], 14, 299; Döpping, *Annalen*, 1843, 46, 172. See also Manuelli, *Atti R. Accad. Lincei*, 1906, [v.], 15, i., 703. For the reaction system $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 - \text{Fe} - \text{S}$, see Jorissen and Kayser, *Zeitsch. physikal. Chem.*, 1927, 130, 482.

⁷ Brückner, *Monatsh.*, 1906, 27, 49.

⁸ Filhol and Senderens, *Compt. rend.*, 1881, 93, 152; Vortmann and Padberg, *Ber.*, 1889, 22, 2642; Selezner, *J. Russ. Phys. Chem. Soc.*, 1882, 1, 124; *Ber.*, 1882, 15, 1191. See also Euler, *Ber.*, 1904, 37, 1704.

⁹ See p. 49.

¹⁰ Moissan, *Compt. rend.*, 1901, 132, 510; Ruff and Geisel, *Ber.*, 1905, 38, 2659; Ruff and Hecht, *Zeitsch. anorg. Chem.*, 1911, 70, 49; Ruff, *Verh. Ges. deut. Naturforsch. Aerzte*, 1911, 11, 24.

formation of hydrogen sulphide and nitrogen sulphide.¹ Aqueous solutions of ammonia resemble solutions of the ordinary alkalis in their action on sulphur, but are less rapid in their effect.²

As has already been mentioned when discussing the allotropy of the element, especially in the gaseous condition, sulphur can exist as molecular aggregates of variable magnitude, so that the molecular weight is not constant and in the gaseous condition ranges actually from S_8 to S . In the molten condition it is probable that at least two types of molecules exist, namely S_8 and S_6 (see pp. 14, 17), but in solution at the ordinary temperature sulphur appears to be present almost entirely as S_8 molecules, even with such a variety of solvents as bromoform,³ iodine,⁴ anthraquinone,⁵ white phosphorus,⁶ antimony trichloride,⁷ carbon disulphide,⁸ carbon tetrachloride,⁹ naphthalene,¹⁰ toluene,¹¹ dimethylaniline¹² and rubber.¹³ The various investigations carried out with solutions of sulphur in these liquids include cryoscopic and ebullioscopic measurements, and measurements of vapour pressure, and from the results obtained the evidence for the existence of octa-atomic sulphur in the dissolved condition is overwhelming.

THE VALENCY OF SULPHUR.

The valency of sulphur is also variable, having in different compounds the values 2, 4 and 6. At one time the existence of 6-valent sulphur

was denied and the formula of sulphuric acid was written $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{S}(\text{OH})_2 \end{array}$

with 4-valent sulphur; the isolation of sulphur hexafluoride, SF_6 , however, proved the possibility of 6-valent sulphur and removed the imaginary obstacle to representing sulphuric acid and sulphur trioxide as derivatives of 6-valent sulphur.¹⁴ By investigation of the physical

¹ Ruff and Geissel, *loc. cit.*; Lebeau and Damoiseau, *Compt. rend.*, 1907, 144, 1422.

² Jones, *Trans. Chem. Soc.*, 1876, 29, 641; Senderens, *Compt. rend.*, 1887, 104, 58; Bloxam, *Trans. Chem. Soc.*, 1895, 67, 277.

³ Borgo and Amadori, *Atti R. Accad. Lincei*, 1900, [v.], 18, 1, 138.

⁴ Ohlvari, *ibid.*, 1908, [v.], 17, ii., 512; Orloff, *J. Russ. Phys. Chem. Soc.*, 1903, 35, 462; Beckmann and Hanshan, *Zeitsch. anorg. Chem.*, 1912, 80, 221.

⁵ Beckmann and Hanshan, *loc. cit.* ⁶ Gloss, *J. Physical Chem.*, 1898, 2, 421.

⁷ Tolloczko, *Bull. Acad. Sci. Cracow*, 1901, 1.

⁸ Beckmann, *Zeitsch. physikal. Chem.*, 1890, 5, 76; Helff, *ibid.*, 1893, 12, 200; Guglielmo, *Atti R. Accad. Lincei*, 1893, [v.], 1, 210; Aronstein and Meihuizen, *Zeitsch. physikal. Chem.*, 1899, 30, 153; Pekar, *Zeitsch. physikal. Chem.*, 1901, 39, 448; Timofejeff, *J. Russ. Phys. Chem. Soc.*, 1903, 35, 644; Orndorff and Terrasse, *Zeitsch. physikal. Chem.*, 1896, 21, 310.

⁹ Odo and Serra, *Gazzetta*, 1899, 29, 2, 243.

¹⁰ Hertz, *Zeitsch. physikal. Chem.*, 1890, 6, 358; also Gloss, *loc. cit.*

¹¹ Orndorff and Terrasse, *loc. cit.*

¹² Popoff, *J. Russ. Phys. Chem. Soc.*, 1903, 35, 642.

¹³ Kelly and Ayers, *Ind. Eng. Chem.*, 1924, 16, 148. See also Biltz, *Zeitsch. physikal. Chem.*, 1897, 19, 425; Barnes, *J. Physical Chem.*, 1899, 3, 156. For determinations of the solubility of sulphur in organic liquids, see Hildebrand and Jenks, *J. Amer. Chem. Soc.*, 1921, 43, 2172; Delaplace, *J. Pharm. Chim.*, 1922, [vii.] 26, 139.

¹⁴ See Krüger, *J. prakt. Chem.*, 1876, [ii.], 14, 193; Nasini and Scala, *Gazzetta*, 1888, 18, 62; *Ber.*, 1888, 21, 586; Klinger and Maassen, *Ber.*, 1888, 21, 94; 1889, 22, 648; Brjuchonensko, *Ber.*, 1898, 31, 3176; Vanzetta, *Gazzetta*, 1900, 30, 1, 175; Divers, *Trans. Chem. Soc.*, 1885, 47, 213. For physico-chemical evidence of variable valency, see Mathews, *J. Physical Chem.*, 1913, 17, 331; Stark and Künzer, *Ann. Physik*, 1914, [iv.], 45, 29.

properties of many organic compounds containing sulphur in a known condition of valency, it has been possible to calculate the part played by the sulphur atom in contributing to such physical properties as the specific gravity and the specific refractivity of its compounds, and hence to attribute to sulphur a fairly definite "atomic volume," "atomic refractivity," etc., for each state of valency.¹

A notable contribution rendered by organic chemistry to our knowledge of the quadrivalent sulphur atom is the demonstration that not only are the four valencies inter-equivalent but they are disposed spatially and not in one plane. The arrangement of these valencies must be analogous to the well-known disposition of the four valencies of the carbon atom, and the quadrivalent sulphur atom, at least in organic compounds, may be regarded as at the centre of a tetrahedron towards the angles of which the four valencies are directed. Such a configuration of the sulphur atom is proved by the existence of two stereo-isomeric forms (enantiomorphous forms) of compounds in which the letters A, B, C, D (fig. 3) represent different radicals. Although the isomerides exhibit similar chemical properties, they exert on polarised light a rotating effect which is equal in extent but opposite in direction. It will be observed that the two spatial formulæ represented in fig. 3, although very similar, are not superposable. The

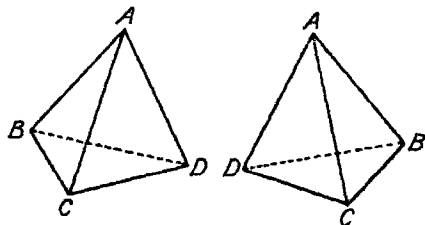


FIG. 3.—Configurations of Enantiomorphous Sulphur Compound.

"sulphonium salts" of the type
$$\begin{array}{c} \text{C}_2\text{H}_5 \\ \text{CH}_3 \end{array} \text{S} \begin{array}{c} \text{CH}_2\text{CO}_2\text{H} \\ \text{X} \end{array}$$
, where X

represents a suitable acid radical, exist as two enantiomorphous isomerides which differ mainly in the direction of their effect on the plane of polarisation of a beam of polarised light.² For the satisfactory explanation of such isomerides a "solid" formula is essential.

THE ATOMIC WEIGHT OF SULPHUR.

That the atomic weight of sulphur is approximately 32 and not a multiple or sub-multiple of this figure is evident from the following considerations :

¹ For atomic volumes, see Kopp, *Annalen*, 1855, 96, 153, 303; Thorpe, *Trans. Chem. Soc.*, 1880, 37, 327; Ramsay, *Ber.*, 1879, 12, 1024; 1880, 13, 2147; Traube, *Ber.*, 1895, 28, 2722; Donath and Mayrhofer, *Ber.*, 1883, 16, 1588; Kannonnikoff, *J. Russ. Phys. Chem. Soc.*, 1902, 34, 575. For atomic refractivity, etc., see Delépine, *Ann. Chim. Phys.*, 1912, [viii.], 25, 529; Gladstone, *Proc. Roy. Soc.*, 1887, 42, 401; Nasini and Costa, *Zeitsch. physikal. Chem.*, 1892, 9, 638; Nasini and Carrara, *ibid.*, 1895, 17, 539; Kannonnikoff, *J. Russ. Phys. Chem. Soc.*, 1884, 1, 119; Hertlein, *Zeitsch. physikal. Chem.*, 1896, 19, 306; Price and Twiss, *Trans. Chem. Soc.*, 1912, 101, 1259. For effect of sulphur on the boiling-point of its compounds, see Delépine, *Compt. rend.*, 1911, 153, 725.

² Pope and others, *Trans. Chem. Soc.*, 1900, 77, 1072; 1902, 81, 1552; Smiles, *ibid.*, 1900, 77, 1174; 1905, 87, 450. For the influence of the sulphur atom on optical rotatory power, see Hilditch, *Trans. Chem. Soc.*, 1908, 93, 1618; Shukla, *J. Indian Inst. Sci.*, 1927, 16 A, 33. For the influence of the sulphur atom on the reactivity of adjacent atoms or groups in organic molecules, see Bennett and Hock, *J. Chem. Soc.*, 1927, p. 477; Bennett and Berry, *ibid.*, 1927, p. 1676.

(i). The specific heat of rhombic sulphur between 28° and 92° C. is 0.1759.¹ Assuming a mean atomic heat of 6.4, by Dulong and Petit's Law the atomic weight is approximately 36.

(ii). Experiment shows that, if Avogadro's hypothesis be accepted, sulphur is never present in its volatile compounds in an amount less than 32 grams per gram-molecule.

(iii). Sulphur, with an atomic weight of 32, fits naturally into the periodic scheme.

(iv). The atomic number of sulphur (16) places the element between phosphorus (15) and chlorine (17), so that its atomic weight should lie between 31 and 35.5.

(v). The mass spectrum shows that three isotopes of sulphur exist, namely 32, 33 and 34. S_{34} is about three times as abundant as S_{33} , and the two together probably amount to about 3 per cent. of the whole.²

The exact atomic weight of sulphur has been determined in two different ways, namely :

1. By gasometric methods.
2. By gravimetric methods.

(1) *Gasometric Methods*.—Only the most recent of these are of sufficient accuracy to lend themselves for useful atomic weight determination, and even then, owing to the uncertainty of the corrections to be applied in view of the fact that the gases concerned do not strictly obey the gas laws, the results cannot be regarded as equal in accuracy to those obtained by gravimetric methods. The best result would appear to be that calculated³ from the density of sulphur dioxide and its compressibility, as determined by Jaquerod and Scheuer, namely $S = 32.059$.⁴

(2) *Gravimetric Methods*.—The early determinations, down to the time of Stas, are now of historical interest only. They are therefore included without further comment in the accompanying table.⁵ In the first series of Stas' experiments a known weight of silver was heated in the vapour of sulphur or in a current of pure hydrogen sulphide. Excess sulphur was removed by distillation in a current of carbon dioxide, the latter having been purified with exceptional care, as traces of impurity in the gas might cause grave error. As a mean of five results, calculated to vacuum, Stas found :

$$2\text{Ag} : \text{Ag}_2\text{S} = 100 : 114.8522 \pm 0.0007,$$

whence the atomic weight of sulphur is 32.045.

By reducing silver sulphate in a current of hydrogen Stas also determined the ratio :

$$\text{Ag}_2\text{SO}_4 : 2\text{Ag} = 100 : 69.208,$$

as a mean of six results, whence the atomic weight of sulphur is 32.022.

These values are too low.

¹ Kurbatoff, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 311.

² Aston, *Nature*, 1926, 117, 893.

³ Wourtsel, *J. Chim. phys.*, 1920, 18, 142.

⁴ Jaquerod and Scheuer, *Mem. Soc. Phys. Hist. Nat. Geneva*, 1908, 35, 675.

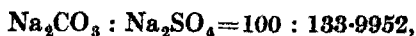
⁵ The values for the atomic weights used here are not necessarily those given originally by the authors, but have been recalculated using the following antecedent data: O = 16.000; Ag = 107.880; Cl = 35.457; N = 14.008; C = 12.000; Na = 22.996.

THE ATOMIC WEIGHT OF SULPHUR.

Year.	Authority.	Ratio Determined.	No. of Expts.	Atomic Weight of Sulphur.
1820	Berzelius (<i>Lehrbuch der Chemie</i> , 5th ed., 1845).	Pb : PbSO ₄	..	32.1
		2Ag : Ag ₂ S	..	32.2
		2AgCl : Ag ₂ S	..	32.6
1833	Turner (<i>Phil. Trans.</i> , 1833, 123, 527).	Pb : PbSO ₄	..	32.1
		PbO : PbSO ₄	..	32.1
		BaO : BaSO ₄	..	32.2
1848	Svanberg and Struve (<i>J. prakt. Chem.</i> , 1848, 44, 320).	2AgCl : Ag ₂ S	..	32.1
1851	Struve (<i>Annalen</i> , 1851, 80, 203).	Ag ₂ SO ₄ : 2Ag	..	31.9
1858	Dumas (<i>Ann. Chim. Phys.</i> , 1858, 55, 146; <i>Annalen</i> , 1858, 105, 86; 1860, 113, 24).	Ag ₂ S : 2Ag, = 100 . 87 0902	5	31.98
1860	Stas (<i>Œuvres Complètes</i> (Brussels), 1894, I., 349, 410).	Ag ₂ S : 2Ag, = 100 : 87.06896	5	32.04
		Ag ₂ SO ₄ : 2Ag, = 100 . 69.20325	6	32.02
1878	Cooke * (<i>Proc. Amer. Acad.</i> , 1878, 13, 52).	Ag ₂ S : 2Ag, = 100 : 87.04124	5	32.12
		Ag ₂ S : 2Ag, = 100 . 87.0953	2	31.97
1891	Richards (<i>ibid.</i> , 1891, 26, 240).	Na ₂ CO ₃ : Na ₂ SO ₄ , = 100 . 133.9855	8	32.021
1907	Richards and Jones (<i>Carnegie Institution, Washington, Publication</i> 69).	2AgCl : Ag ₂ SO ₄ , = 100 : 108.7745	10	32.068
1911	Burt and Usher (<i>Proc. Roy. Soc.</i> , 1911, [A], 85, 82).	2N ₂ : N ₄ S ₈ , = 100 : 328.9021	7	32.065
1915	Richards and Hoover (<i>J. Amer. Chem. Soc.</i> , 1915, 37, 1., 95, 108). See also Moles (<i>J. Chim. phys.</i> , 1917, 15, 51); Guye (<i>ibid.</i> , p. 60).	Na ₂ CO ₃ : Na ₂ SO ₄ , = 100 : 134.0158	6	32.054

* These experiments were merely incidental to Cooke's researches on the atomic weight of antimony.

Turning now to more recent work, mention may be made of that of Richards. Three of the eight determinations of the ratio Na₂CO₃ : Na₂SO₄ made by Richards in 1891 were somewhat doubtful. Omitting these, the mean ratio for the remaining five experiments becomes :



whence $S=32.032$. This value, however, is still slightly too low. Re-determination of the same ratio by Richards and Hoover in 1915 gave $S=32.054$, and this agrees with the value $S=32.059$ determined by volumetric methods.

It is difficult to understand why the foregoing values should still be so much lower than that determined by Richards in 1907 from the ratio $2\text{AgCl} : \text{Ag}_2\text{SO}_4$, namely 32.068, for this latter value agrees closely with the 32.065 derived by Burt and Usher in 1911 from the ratio $2\text{N}_2 : \text{N}_4\text{S}_4$ (see table). The value accepted by the "International Atomic Weights Commission" in 1925 was 32.064, whilst the Revised Table for 1929 published by the Council of the Chemical Society¹ gives the value 32.06(5), in which the last figure may be in error by two or three units.

THE DETECTION AND ESTIMATION OF SULPHUR.

Detection.—Sulphur in the free state is readily recognisable by its general appearance and characteristics, and especially by its combustion to sulphur dioxide. Both in mixtures and compounds the presence of the element can be demonstrated by heating with charcoal and an alkali carbonate,² or even better, on a small scale, by heating with an equal bulk of sodium or potassium,³ or with powdered iron;⁴ in each case some of the sulphur is converted into sulphide, which may be detected by the action of an aqueous extract on mercury or silver, or on sodium nitroprusside; the metals are blackened, whilst the nitroprusside is very sensitive in giving a purple coloration (see p. 62). Alternatively, the solution of the alkali sulphide may be acidified and tests applied for hydrogen sulphide to the vapours evolved on warming.

Various microchemical tests are available for the detection of minute quantities of sulphur, both free and combined. The substance under examination may be treated with a little sodium hydroxide solution, the extract evaporated just to dryness, a few drops of aqueous sodium cyanide (0.1 per cent.) added and the evaporation repeated. The residue, moistened with dilute sulphuric acid and a drop of ferric chloride, gives the characteristic ferric thiocyanate colour if sulphur is present.⁵ In the case of minerals, traces of sulphur dioxide produced on heating may be detected⁶ by the colour change of an alkaline solution of Bromocresol Green or by the decolorisation of starch-iodine solution.

A micro-test for organically combined sulphur in plants consists⁷ in exposing the material to bromine vapour for several hours in order to bring about oxidation. After removing excess of bromine by means of ammonia or by volatilisation, the sulphate is precipitated by calcium chloride, the crystalline precipitate being examined on the following day.

Estimation.—Free sulphur is often estimated by extraction with carbon disulphide,⁸ especially where a distinction is to be made from

¹ *J. Chem. Soc.*, 1929, p. 218.

² Bailey, *Amer. J. Sci.*, 1851, [ii.], 11, 351.

³ Vohl, *Zeitsch. anal. Chem.*, 1863, 2, 442.

⁴ Noll, *Farben-Zig.*, 1928, 33, 1849; *Papier Fabr.*, 1928, 26, Fest- u. Auslands-Heft, 59.

⁵ Grunsteidl, *Zeitsch. anal. Chem.*, 1929, 77, 283.

⁶ Roberts and Selchow, *Amer. J. Sci.*, 1928, [v.], 15, 455.

⁷ Klein, *Oesterr. bot. Zeit.*, 1927, 76, 15; *Chem. Zentr.*, 1927, ii., 2329.

⁸ Frühling, *Zeitsch. angew. Chem.*, 1889, p. 242.

combined sulphur. Total sulphur is usually determined by oxidation to sulphuric acid, the latter being weighed as barium sulphate.¹ The oxidising agents commonly applied are bromine water, nitric acid, perchloric acid, potassium nitrate, potassium chlorate and sodium peroxide;² the last three are usually mixed with anhydrous sodium carbonate and applied by fusion; they are suited to the estimation of sulphur in organic compounds.³

In the estimation of sulphur in organic compounds by oxidation with nitric acid, the acid is sometimes mixed with bromine⁴ or an alkali chloride,⁵ or, more frequently, fuming nitric acid is used,⁶ in which case the oxidation is commonly effected in a sealed glass tube at 150° to 300° C.⁷ A very convenient electrolytic apparatus (fig. 4) has, however, been described,⁸ in which only ordinary concentrated nitric acid is necessary; the lower electrode is the anode, and the bubbles of gas, escaping periodically from beneath the concave surface, cause sufficient agitation and stirring. The great advantage of such a method as this is its safety, the oxidation proceeding at the ordinary pressure, although requiring no longer time than the sealed-tube method.

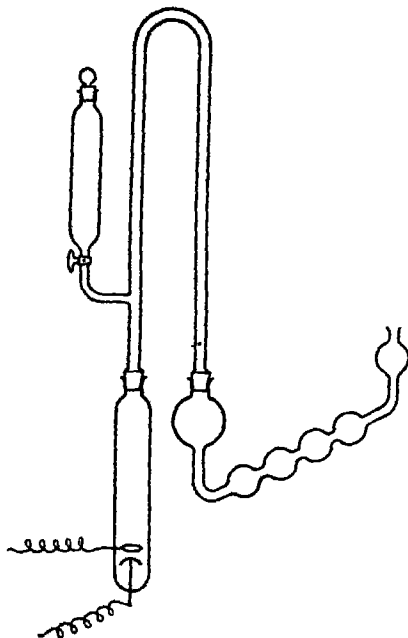


FIG. 4.—Electrolytic Apparatus for Determination of Sulphur in Organic Compounds.

Whenever nitric acid or a nitrate has been used for the oxidation, it is advisable to remove excess by evaporation with hydrochloric acid before proceeding to the precipitation of the sulphuric acid with barium chloride.⁹

Another method applicable to organic compounds consists in com-

¹ For the use of the centrifuge in separating the barium sulphate, see Gunder, *Zeitsch. anal. Chem.*, 1928, 73, 441.

² Hempel, *Zeitsch. anorg. Chem.*, 1893, 3, 193; Clark, *Trans. Chem. Soc.*, 1893, 63, 1079; Drown, *Chem. News*, 1881, 43, 89; Bjerregaard, *J. Ind. Eng. Chem.*, 1919, 11, 1055; Gebauer-Fulnegg and Petertil, *Monatsh.*, 1927, 48, 619; Kahane, *Caoutchouc et Gutta-percha*, 1926, 23, 13, 154; 1927, 24, 13, 549.

³ For a comparative test of five oxidation methods, see Smith and Bain, *Canadian Chem. Met.*, 1928, 12, 287.

⁴ De Koninck, *Bull. Acad. roy. Belg.*, 1871, [n.], 32, 11; Tuttle and Isaacs, *J. Ind. Eng. Chem.*, 1915, 7, 658; *Chem. News*, 1916, 114, 88.

⁵ See Rogers and Dougherty, *J. Amer. Chem. Soc.*, 1928, 50, 1231.

⁶ Lefort, *Zeitsch. anal. Chem.*, 1873, 12, 32.

⁷ Carius, *Annalen*, 1860, 116, 11, 28; 1865, 136, 129; *Ber.*, 1871, 3, 697.

⁸ Gasparini, *Gazzetta*, 1907, 37, 426; *J. Soc. Chem. Ind.*, 1908, 27, 340.

⁹ For details of the various methods by which sulphur can be estimated, standard books of reference should be consulted; e.g. Treadwell and Hall, *Analytical Chemistry* (Wiley & Sons), 1924; Scott, *Standard Methods of Chemical Analysis* (van Nostrand, N.Y.), 1918; Lunge and Keane, *Technical Methods of Chemical Analysis* (Gurney & Jackson), 1914.

pletely converting the sulphur into hydrogen sulphide.¹ The substance is vaporised or decomposed by heating in a current of hydrogen and the mixture of vapours and hydrogen then passed through a heated quartz tube containing platinised asbestos. The resulting hydrogen sulphide is absorbed in alkali and estimated iodometrically.

A rapid volumetric method for the determination of sulphur is as follows:² The sulphur is dissolved in a known volume of hot standard sodium hydroxide solution and after cooling is oxidised to sulphate by the addition of hydrogen peroxide; the excess of alkali is then titrated with standard acid.³ The method is applicable to gases containing any common sulphur compound except thiophen (*e.g.* coke oven gas).⁴

The sulphur content of coals, oils, tars, asphalts, etc., may be determined by combustion in an oxygen bomb, a little ammonium nitrate being added to the charge to ensure complete oxidation to sulphuric acid (see p. 136).⁵ After washing out the bomb the sulphur is determined as barium sulphate.

¹ ter Meulen, *Rec. Trav. chim.*, 1922, 41, 112. See also Losana, *Gorn. Chim. Ind. Appl.*, 1922, 4, 204; Récssei, *Chem. Zeit.*, 1926, 50, 785; 1927, 51, 96; Eigenberger, *Zeitsch. anal. Chem.*, 1926, 68, 220.

² Kuhl, *Zeitsch. anal. Chem.*, 1924, 65, 185.

³ For a summary of methods for the estimation of sulphur in iron and steel, see Pulsifer, *J. Ind. Eng. Chem.*, 1916, 8, 1115. See also Zschuegner, *ibid.*, 1916, 8, 324; Marriot, *Ann. Chim. anal.*, 1922, [ii.], 4, 5; Nikolai, *Chem. Zeit.*, 1922, 46, 1025; Ashida, *J. Soc. Chem. Japan*, 1923, 44, 483; Kitajima, *Rikwagaku Kenkyujo Iho*, 1923, 2, 243; Järvinen, *Zeitsch. anal. Chem.*, 1926, 68, 397; Kling and Lassieur, *Chem. Ind.*, 1926, 15, 699; Ciocchina, *ibid.*, 1927, 17, 383; *Zeitsch. anal. Chem.*, 1927, 72, 301; Marquoyrol and Toquet, *Ann. Chim. anal.*, 1927, [ii.], 9, 225; Steinmetz, *Ind. Eng. Chem.*, 1928, 20, 983; Swoboda, *Zeitsch. anal. Chem.*, 1929, 77, 269. See also *Chemical Age*, 1929, 20, 3. For the estimation of sulphur in roasted ores, see Pérégryn, *Ann. Chim. anal.*, 1917, 22, 26, in soils, Simon and Schollenberger, *Soil Sci.*, 1925, 20, 393; in lead, Evans, *Analyst*, 1927, 52, 565; Leysaht, *Zeitsch. anal. Chem.*, 1929, 77, 209; in antimony, Snyder, *Chemist-Analyst*, 1929, 18, 6; in biological materials, Drummond, *Biochem. J.*, 1915, 9, 492; Pohorecka-Lelesz, *Bull. Soc. chim. biol.*, 1927, 9, 263; Konarsky, *Biochem. Zeitsch.*, 1927, 187, 398; Lesure and Dunez, *Bull. Soc. chim. biol.*, 1928, 10, 879; 1929, 11, 600; in vulcanised rubber, Eaton and Day, *J. Soc. Chem. Ind.*, 1917, 36, 16; Dyer and Watson, *ibid.*, 1922, 41, 251; Kahane, *Caoutchouc et Gutta-percha*, 1926, 23, 13, 154; 1927, 24, 13, 549; *Ann. Chim. anal.*, 1927, [ii.], 9, 261; Wolesensky, *Ind. Eng. Chem.*, 1928, 20, 1234; Mackay, *J. Soc. Chem. Ind.*, 1930, 49, 233 T. For microchemical methods applicable to organic substances, see Hanai, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1928, 7, 915; Kubota and Hanai, *Bull. Chem. Soc. Japan*, 1928, 3, 168; Hein, Hoyer and Klar, *Zeitsch. anal. Chem.*, 1928, 75, 161; Lucas and Grassner, *Mikrochem.*, 1928, 6, 116.

⁴ Heinrich and Petzold, *Zeitsch. anal. Chem.*, 1929, 76, 120.

⁵ Bradley, Corbin and Floyd, *Ind. Eng. Chem.*, 1926, 18, 583. See also Kohout, *ibid.*, 1927, 19, 1065; Woodward, *ibid.* (Anal.), 1929, 1, 117; Griffin, *ibid.*, p. 167; de Fazi, *Annali Chim. Appl.*, 1926, 16, 405. See further on the determination of sulphur in solid fuels, Schön and Vykypěl, *Chem. Zeit.*, 1926, 50, 673; Bahr and von der Heide-Melzer, *Brennstoff-Chem.*, 1926, 7, 313; Tykač and Streit, *Chem. Zentr.*, 1928, i, 1123; Hackl, *Chem. Zeit.*, 1928, 52, 933; Nikolai and Vorobiev, *Izvestia Teplotekh. Inst. Moscow*, 1929, No. 3, 91; in oils, Hauser, *Anal. Fis. Quim.*, 1921, 19, 175; Wagner, *Zeitsch. angew. Chem.*, 1923, 36, 494; 1925, 38, 1068; in petroleum, Francis and Crawford, *J. Ind. Eng. Chem.*, 1917, 9, 479; Faragher, Morrell and Monroe, *Ind. Eng. Chem.*, 1927, 19, 1281; Kennedy, *ibid.*, 1928, 20, 201; Korsakov, *Neft. Khoz.*, 1928, 14, 68; Devine and Lane, *J. Amer. Chem. Soc.*, 1928, 50, 1707; in benzole, Ormandy and Craven, *J. Inst. Petrol. Tech.*, 1925, 11, 556; in coal gas, Mylius and Hüttner, *Ber.*, 1916, 49, 1428; in spent gas purifying material, Stavorinus, *Gas- u. Wasserfach*, 1926, 69, 790.

CHAPTER III.

COMPOUNDS OF SULPHUR.

ALTHOUGH sulphur in the compact form appears to be a comparatively inactive element, yet when in a fine state of division it reacts with many metals, and at elevated temperatures it combines directly with nearly all other elements (exceptions being nitrogen, iodine, beryllium, gold, platinum and iridium) to form stable binary compounds, the reactions often occurring with great vigour.

In its most stable compounds with hydrogen and the metals, sulphur is usually bivalent, but it possesses the property of combining with these elements in proportions exceeding the valency requirements, forming series of polysulphides of the type R_2S_x , where x may be as high as 6 (see p. 67). The polysulphides of hydrogen are unstable oily liquids of uncertain freezing-points, and on heating undergo decomposition.

Towards the halogens, sulphur is electropositive. Combination with fluorine and chlorine takes place at ordinary temperatures, the product in the former case being the hexafluoride, SF_6 , whilst with chlorine, sulphur monochloride, S_2Cl_2 , is first formed, then the dichloride, SCl_2 , and finally the tetrachloride, SCl_4 . A monofluoride and a monobromide are also known, but no compound of sulphur and iodine has been isolated.

Sulphur is also electropositive towards oxygen, and in the oxides and their derivatives the element usually exhibits a valency of 4 or 6. The two stable oxides, SO_2 and SO_3 , are strongly acidic, giving rise to sulphurous and sulphuric acids, respectively, from which numerous other oxyacids are derived. An intermediate unstable sesquioxide, S_2O_3 , is known, but it does not appear to be the anhydride of hydrosulphurous acid, $H_2S_2O_4$, as its formula would suggest, since this acid cannot be obtained from it. Products have also been described purporting to contain a higher oxide variously formulated as S_2O_7 , SO_4 and S_3O_{11} (see pp. 180, 188), from which the peracids are derived, but the identity of such an oxide has not yet been satisfactorily established.

The following is a list of the oxyacids of sulphur; those in brackets are only known in the form of their derivatives, whilst those marked with an asterisk are known in solution, but have not been isolated:

- (Sulphoxylic acid, H_2SO_2).
- *Hydrosulphurous acid, $H_2S_2O_4$.
- *Sulphurous acid, H_2SO_3 .
- Sulphuric acid, H_2SO_4 .
- Pyrosulphuric acid, $H_2S_2O_7$.
- *Thiosulphuric acid, $H_2S_2O_3$.
- Permonosulphuric acid, H_2SO_5 .

Perdisulphuric acid, $\text{H}_2\text{S}_2\text{O}_8$.

*Dithionic acid, $\text{H}_2\text{S}_2\text{O}_6$.

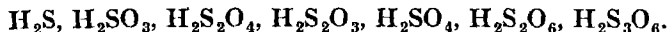
*Trithionic acid, $\text{H}_2\text{S}_3\text{O}_6$.

*Tetrathionic acid, $\text{H}_2\text{S}_4\text{O}_6$.

*Pentathionic acid, $\text{H}_2\text{S}_5\text{O}_6$.

(Hexathionic acid, $\text{H}_2\text{S}_6\text{O}_6$).

Arranged in order of increasing strength, the sulphur acids are as follows :



Hydrogen sulphide is the weakest acid, di- and tri-thionic acids are approximately of equal strength, whilst sulphurous acid is the weakest oxyacid in the list.¹

On replacement of one hydroxyl group in sulphuric acid, $\text{SO}_2(\text{OH})_2$, by such univalent radicals as $-\text{NH}_2$, $-\text{NO}_2$, $-\text{F}$ or $-\text{Cl}$, a series of sulphonic acids may be obtained, from which a large number of derivatives, both inorganic and organic, have been prepared (see, for example, pp. 242-252).

The compounds of sulphur with nitrogen and carbon and their more important derivatives are described in this volume, pp. 233-285; the compounds with phosphorus are described under the latter element in Vol. VI., Part II.

SULPHUR AND HYDROGEN.

The most important and the most stable compound of sulphur and hydrogen is the well-known hydrogen sulphide, but, in addition, at least three well-defined compounds, H_2S_2 , H_2S_3 and H_2S_5 , are known, and there is evidence that a hexasulphide, H_2S_6 , also exists.

Hydrogen Sulphide, Sulphuretted Hydrogen or Hydrosulphuric Acid, H_2S .

Occurrence.—Hydrogen sulphide is present in volcanic gases,² probably owing to the action of steam on sulphides or sulphur at a high temperature in the earth. It is also found in the waters of certain spas,³ as for example Harrogate and Strathpeffer in this country and Aix-les-Bains on the Continent: the hydrogen sulphide of such "sulphurous" waters has probably been formed at least in part by the biochemical reduction of mineral sulphates⁴ (see p. 175). Not many bacteria able to reduce sulphates are known, however, and those that are known are non-sporogenic and strictly anaerobic. The reducing action appears to be associated with the oxidation of organic matter,

¹ Jellinek, *Zeitsch. physikal. Chem.*, 1911, 76, 257; Kolthoff, *Rec. Trav. chim.*, 1924, 43, 216.

² Phillips, *J. Amer. Chem. Soc.*, 1898, 20, 696; see also Harrington, *Amer. J. Sci.*, 1904, 19, [iv.] 345.

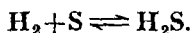
³ Liebig, *Annalen*, 1851, 79, 94; Meyer, *J. prakt. Chem.*, 1862, 91, 1; Fresenius, *Ber.*, 1877, 10, 688; Garrigou, *Compt. rend.*, 1874, 79, 487, 541, 683; Filhol, *ibid.*, 1874, 79, 610; Gautier, *ibid.*, 1901, 132, 740.

⁴ Thomann, *Schweiz. Woch. Pharm.*, 1906, 44, 5; *Abstr. Chem. Soc.*, 1906, 90, ii., 477; see also Burghardt, *Chem. News*, 1878, 37, 49.

whence the necessary energy is derived.¹ Decomposing organic matter, especially of animal origin, also frequently gives rise to hydrogen sulphide, due to the decomposition of the albuminoid substances under the influence of micro-organisms.

History.—The fact that sulphur is soluble in aqueous solutions of alkaline substances was known to the alchemists, who realised that it could again be liberated by acidifying, but although the simultaneous liberation of a "sulphurous air" is mentioned in their records, the gas was not submitted to careful examination. During the phlogistic period the combustibility of the gas was discovered as well as its precipitant action on solutions of metallic salts. In 1777, Scheele obtained it by the action of acids on calcium polysulphide and also on manganese sulphide and ferrous sulphide; he observed the solubility of the gas in water and its oxidation to free sulphur by atmospheric air and other oxidising agents. On account of the phlogistic views prevalent at the time, however, Scheele and his contemporaries failed to recognise the real nature of the gas, which received such names as "liver of sulphur air," "hepatic air." The gas was first recognised as an oxygen-free acid by Berthollet in 1796.²

Formation and Preparation.—1. *From its Elements.*—(a) Above 200° C. hydrogen and sulphur interact with appreciable velocity, forming hydrogen sulphide.³ Below 350° C. the combination proceeds slowly until one or other of the reagents is entirely consumed, but above this temperature, although the reaction is naturally more rapid, the final product is an equilibrium mixture, the change being representable thus :



The higher the temperature the lower the proportion of hydrogen sulphide in the equilibrium mixture.

A careful examination of the velocity of the reaction under varied conditions indicates that it is proportional to the pressure of the hydrogen and to the square root of the pressure of the sulphur vapour ;⁴ this result is interpreted as due to the reaction occurring in stages, the first being a slow, reversible change, $\text{S}_8 \rightleftharpoons 4\text{S}_2$, followed by a very rapid dissociation, $\text{S}_2 \rightleftharpoons 2\text{S}$, the combination of molecular hydrogen and atomic sulphur then proceeding with measurable velocity. Platinum black or red phosphorus accelerates the combination,⁵ as also does exposure to ultra-violet light.

The formation of hydrogen sulphide in this manner can be realised experimentally by passing hydrogen or even purified coal gas into sulphur boiling in a flask, when the issuing gas will contain appreciable quantities of hydrogen sulphide.⁶ Under pressures of 5 to 10 atmo-

¹ Eliot, *Ind. Eng. Chem.*, 1927, 19, 1368.

² Berthollet, *Ann. Chim. Phys.*, 1798, 25, 233. For a detailed historical account, see Kopp, *Geschichte der Chemie*, 1845, 3, 317.

³ Correnwinder, *Ann. Chim. Phys.*, 1852, [iii.], 34, 77 ; Cossa, *Ber.*, 1868, 1, 117 ; Merz and Weith, *Ber.*, 1869, 2, 341 ; Chevrier, *Compt. rend.*, 1869, 69, 136 ; Januario, *Gazzetta*, 1880, 10, 46 ; Boillot, *Compt. rend.*, 1870, 70, 97 ; 1873, 76, 628, 869 ; Konowalov, *J. Russ. Phys. Chem. Soc.*, 1898, 30, 371 ; Pélabon, *Compt. rend.*, 1897, 124, 35, 686 ; *J. Chim. Phys.*, 1909, 7, 447.

⁴ Bodenstein, *Zeitsch. physikal. Chem.*, 1899, 29, 315 ; Norrish and Rideal, *Trans. Chem. Soc.*, 1924, 125, 2070.

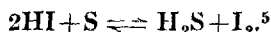
⁵ Milbauer, *Ann. Chim. Phys.*, 1907, [viii.], 10, 126. See also under "Dissociation," p. 55.

⁶ Taylor, *Chem. News*, 1883, 47, 145.

spheres the reaction proceeds at 250° to 300° C., giving a satisfactory yield if the liquid sulphur is subjected to vigorous agitation.¹

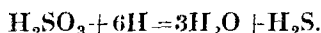
(b) Sulphur can also be reduced to hydrogen sulphide at the ordinary temperature if "nascent" hydrogen is used; thus, powdered sulphur yields some hydrogen sulphide if treated with aluminium, tin, iron or zinc and hydrochloric acid,² the result being improved by the additional presence of acetic acid or alcohol, which will increase the solubility of the sulphur.³ The reduction can also be effected electrolytically by having powdered sulphur in contact with a platinum cathode immersed in dilute acid, e.g. hydrochloric acid.⁴

When heated with hydrogen iodide or concentrated aqueous hydriodic acid, sulphur is reduced to hydrogen sulphide, but once more the reaction is incomplete, leading only to an equilibrium mixture :



Other processes which are known to produce hydrogen sulphide from sulphur include treatment with steam or water⁶ (e.g. in a sealed tube at 200° C. or higher temperature), heating with organic matter⁷ (e.g. a mixture of vaseline with sulphur in the proportions 7 : 3 gives rise to very pure hydrogen sulphide when heated), and the reducing action of certain anaerobic micro-organisms⁸ in the presence of water at the ordinary temperature, as well as ordinary alcoholic fermentation.⁹

2. *From Sulphur-Oxygen Compounds.*—Sulphites in aqueous solution are easily reduced to hydrogen sulphide by nascent hydrogen, produced, for example, by the interaction of zinc and dilute sulphuric acid :



The reduction of sulphites and of sulphates can also be effected by certain bacteria, the presence of hydrogen sulphide in some mineral waters probably being due to reduction of calcium sulphate in this way.¹⁰ The first product is probably the corresponding sulphide, which subsequently undergoes hydrolytic decomposition.

Hydrogen sulphide is also formed when sulphur dioxide is carried

¹ Bacon, *American Patent*, 1700578 (1929).

² Clooz, *Compt. rend.*, 1858, 47, 819.

³ Trautmann, *Bull. Soc. Ind. Mulhouse*, 1891, 87.

⁴ Becquerel, *Compt. rend.*, 1863, 56, 237.

⁵ Hautefeuille, *Ann. Chim. Phys.*, 1858, [iii], 54, 50.

⁶ Correnwinder, *Compt. rend.*, 1861, 53, 140; Gêhs, *ibid.*, 1862, 54, 1014; Girard, *ibid.*, 1863, 56, 797; Gripon, *ibid.*, 1863, 56, 1137; Myers, *J. prakt. Chem.*, 1869, 108, 23; Geitner, *Annalen*, 1864, 129, 350; Böhm, *Ber.*, 1882, 15, 1337.

⁷ Reinsch, *J. prakt. Chem.*, 1838, 13, 142; Fletcher, *Chem. News*, 1879, 40, 154; Johnston, *ibid.*, 1879, 40, 167; Galletly, *ibid.*, 1871, 24, 107; Lidow, *Ber.*, 1881, 14, 1712; Prothière, *L'Union pharm.*, 1902, p. 12; *Abstr. Chem. Soc.*, 1903, 84, ii, 284; Drakeley, *J. Chem. Soc.*, 1917, 111, 853.

⁸ Böhm, *loc. cit.*; Miquel, *Ber.*, 1879, 12, 2152; Debraye and Legrain, *ibid.*, 1891, 24, 466; Paine, *Proc. Iowa Acad. Sci.*, 1925, 32, 63; Almy and James, *J. Bact.*, 1926, 12, 319.

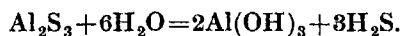
⁹ de Reyl-Pailhade, *Compt. rend.*, 1888, 106, 1683; 107, 43; 1889, 108, 356; Pozzi-Escot, *Bull. Soc. chim.*, 1902, [iii], 27, 692; *Compt. rend.*, 1903, 137, 495; Chowrenko, *Zeitsch. physiol. Chem.*, 1912, 80, 253. See also Abelous and Ribaut, *Compt. rend.*, 1903, 137, 95.

¹⁰ Plauchud, *Compt. rend.*, 1882, 95, 1363; Étard and Olivier, *Ber.*, 1882, 15, 3091; Beijerinck, *Centrabl. Bakteriöl.*, 1900, [ii], 6, 193; Salkowski, *Zeitsch. physiol. Chem.*, 1913, 83, 165; Sasaki and Otsuka, *Biochem. Zeitsch.*, 1912, 39, 208; Will and Schöllhorn, *Zeitsch. ges. Brauw.*, 1905, 23, 285; *Chem. Soc. Abstr.*, 1905, 88, ii, 547; Schander, *Jahresber. Verein angew. Bot.*, 1903-1904, p. 85; *Chem. Soc. Abstr.*, 1905, 88, ii, 647.

in a blast of steam through red-hot coke; the actual reduction is probably effected by hydrogen, since this gas is known to reduce sulphur dioxide at a dull red heat.¹

8. *From Sulphides* (see also p. 63).—Almost all the methods commonly employed for the production of sulphuretted hydrogen belong to this class.

Some sulphides, *e.g.* aluminium sulphide, are decomposed in the cold by water, with liberation of hydrogen sulphide : ²



The sulphides of the alkali metals and of the alkaline earth metals are readily decomposed by weak acids, even by carbonic acid.³ By the use of these sulphides and dilute sulphuric acid it is possible to obtain hydrogen sulphide in a high degree of purity. The hydrosulphides of the alkaline earth metals are convenient sources of hydrogen sulphide, yielding the gas on treatment with carbon dioxide or even by merely heating.⁴ The carbon dioxide method is applied on a technical scale in the extraction of sulphur from alkali waste (see p. 56).

When the gas is intended for ordinary laboratory purposes, ferrous sulphide and hydrochloric acid are the reagents commonly employed for preparing hydrogen sulphide.⁵ The reaction occurs readily at the ordinary temperature, but as the ferrous sulphide is produced by heating together iron and sulphur, it commonly contains at least traces of metallic iron which cause the evolved gas to be contaminated with hydrogen, in addition to impurities such as arsine⁶ due to the presence of impurities in the iron. In order to avoid these impurities the use of precipitated ferrous sulphide has been suggested, but such a process would have various disadvantages in addition to increased cost. Manganese sulphide and zinc sulphide have also been recommended in place of ferrous sulphide.

The chief defects of the ordinary laboratory forms of hydrogen sulphide generators result from the comparative slowness of the reaction between the acid and the sulphide, especially when the concentration of the former is low. The apparatus described below (fig. 5) is more suitable for meeting continuous heavy demands, providing a rapid evolution of the gas from minimum quantities of acid, which undergoes complete neutralisation.⁷ The reaction is brought about at a temperature in the neighbourhood of 100° C. by surrounding the sulphide container with steam; a short air condenser at A ensures practically complete condensation of the outgoing steam, so that little attention is necessary. The acid holders contain commercial hydrochloric acid

¹ Hartmann, *Dingl. Poly. J.*, 1880, 237, 143.

² Fonzes-Diacon, *Bull. Soc. chim.*, 1907, [iv.], i, 36.

³ Finkener, *Ber.*, 1878, 11, 1641; Hampe, *Chem. Zeit.*, 1890, 14, 1777; Fresenius, *Zeitsch. anal. Chem.*, 1887, 26, 339; Winkler, *Zeitsch. anal. Chem.*, 1888, 27, 26; Otto, *Ber.*, 1879, 12, 215; Bong, *Chem. Industrie, Berlin*, 1880, 90; Draper, *Chem. News*, 1884, 50, 292; Habermann, *Zeitsch. angew. Chem.*, 1890, 3, 116; Parnell and Simpson, *Ber.*, 1886, 19, 325; 1888, 21, 804.

⁴ von Miller and Opl, *Ber.*, 1884, 17, 390; Michler, *Chem. Zeit.*, 1897, 21, 659; Divers and Shimidzu, *Chem. News*, 1884, 50, 233.

⁵ Gay-Lussac, *Ann. Chim. Phys.*, 1818, 7, 314. Also this Series, Vol. IX., Part II., p. 134.

⁶ Gautier, *Bull. Soc. chim.*, 1903 [iii.], 29, 867.

⁷ Steele and Denham, *Trans. Chem. Soc.*, 1920, 117, 527.

diluted with an equal volume of water, and when the tap B is first opened, if the sulphide is thoroughly heated reaction takes place with almost explosive violence and each drop of acid is soon completely exhausted. A too sudden entry of acid is prevented by the insertion at D of a piece of capillary tubing, 3 cm. long and 1 mm. bore. In order

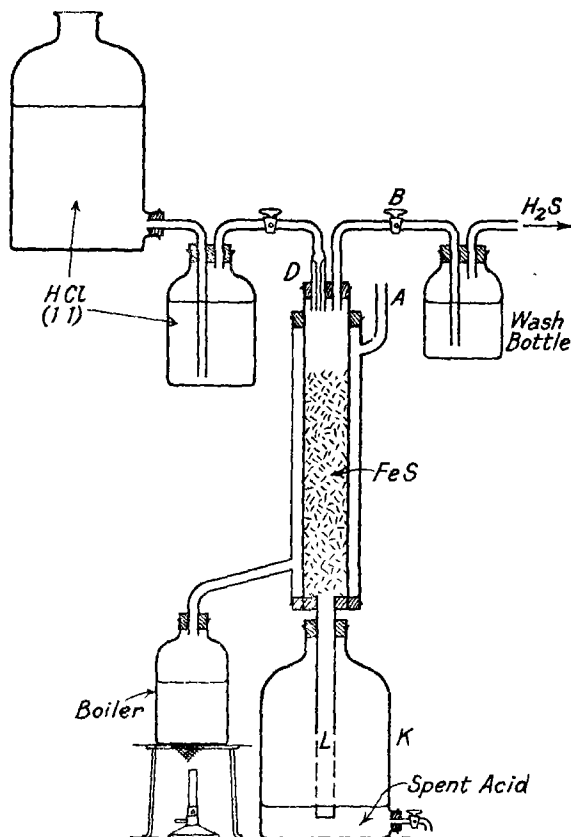
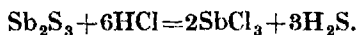


FIG. 5.—Improved Hydrogen Sulphide Generator.

to facilitate the displacement of air from the reservoir K by the incoming spent acid, the tube L has a number of holes blown in it.¹

For the production of hydrogen sulphide free from uncombined hydrogen, the mineral stibnite is frequently used; this reacts with concentrated hydrochloric acid, but the reaction is slow unless aided by warming:



Purification.—The commonest impurities in hydrogen sulphide are free hydrogen and arsine. The latter, which is due to the presence

¹ For a description with diagram of an adaptation of the ordinary Kipp generator for conducting hydrogen sulphide precipitation under pressures of about 100 gms. per cm.², see Fuller, *J. Ind. Eng. Chem.*, 1917, 9, 792. The method is claimed to economise time and material and to produce granular precipitates which filter readily.

of arsenic in the reagents, can be removed by chemical means, for example by passing over heated potassium polysulphide ("liver of sulphur") at $350^{\circ}\text{C}.$,¹ the arsenic being converted into potassium thioarsenate. Other methods of treatment for the removal of arsenic include the action of solid iodine at the ordinary temperature, by which the arsine is converted into arsenic iodide and hydrogen iodide, whilst the hydrogen sulphide passes on almost unaltered and can be freed from hydrogen iodide by washing with water.² Mere passage of the gas through a glass tube packed with glass fragments at a dull red heat is also effective in causing decomposition of the arsine.³

Hydrogen sulphide is generally dried by passage through anhydrous calcium chloride, but as this may lead to the introduction of small quantities of hydrogen chloride, calcium chloride is not so satisfactory a drying agent as phosphoric oxide.

Moissan, in 1903, applied a very elegant method to the removal of all impurities from hydrogen sulphide.⁴ The gas was dried by slow passage through two or three glass tubes at $-50^{\circ}\text{C}.$ to $-70^{\circ}\text{C}.$, which procedure is as effective as the chemical drying agents commonly applied. The hydrogen sulphide was then collected as a solid in a glass tube immersed in liquid air, and any air or free hydrogen present was drawn away by exhausting with a pump. On allowing the mass to warm gradually, it melted, and then attained a state of ebullition, the pure gas being collected when the boiling-point was constant.

Physical Properties.—Hydrogen sulphide is a colourless gas with the unpleasant odour which is commonly associated with a bad egg (see p. 48), the smell of which is actually due largely to this gas. It is 1.189 times as dense as air and one litre at N.T.P. weighs 1.539 grams.⁵

In the formation of hydrogen sulphide from its elements heat is evolved, gaseous hydrogen sulphide when referred to hydrogen gas and solid sulphur being exothermic to the extent of 2.73 Calories per gram-molecule.⁶ The specific heat at constant pressure is 0.2423,⁷ the ratio C_p/C_v at $20^{\circ}\text{C}.$ having the value 1.315.⁸ The heat capacity decreases with increasing temperature.

Water dissolves hydrogen sulphide fairly readily at the ordinary temperature,⁹ the solubility following Henry's Law.¹⁰ Solution is accompanied by an evolution of 4.56 Calories per gram-molecule of gas dissolved.¹¹

¹ Pfordten, *Annalen*, 1886, 234, 257.

² Jacobsen, *Ber.*, 1887, 20, 1999.

³ Gautier, *Bull. Soc. chim.*, 1903, [iii.], 29, 867.

⁴ Moissan, *Compt. rend.*, 1903, 137, 363. See also Cardoso and Arni, *J. Chim. phys.*, 1912, 10, 504.

⁵ Bleekrode, *Proc. Roy. Soc.*, 1884, 37, 339; Leduc, *Compt. rend.*, 1897, 125, 571; Baume and Perrot, *J. Chim. phys.*, 1908, 6, 610.

⁶ Thomsen, *Thermochemische Untersuchungen*, 1882, II., 63; *Ber.*, 1872, 5, 771; 1873, 16, 1535; *Zeitsch. physikal. Chem.*, 1905, 52, 343.

⁷ Croullebois, *Ann. Chim. Phys.*, 1870, [iv.], 20, 136.

⁸ Preuner and Schupp, *Zeitsch. physikal. Chem.*, 1909, 68, 129; Muller, *Ann. Phys. Chem.*, 1883, [iii.], 18, 94; Capstick, *Proc. Roy. Soc.*, 1895, 57, 322; Millar, *J. Amer. Chem. Soc.*, 1923, 45, 874. For the refractive index of gaseous hydrogen sulphide, see Cuthbertson and Cuthbertson, *Proc. Roy. Soc.*, 1910, 83, [A], 171.

⁹ Bunsen and Schönfeld, *Annalen*, 1855, 93, 26; 95, 10; Wiedemann, *Ann. Phys. Chem.*, 1882, [iii.], 17, 349; Prytz and Holst, *Ann. Phys. Chem.*, 1895, [iii.], 54, 130.

¹⁰ McLauchlan, *Zeitsch. physikal. Chem.*, 1903, 44, 600; Porman, *Trans. Chem. Soc.*, 1895, 67, 877.

¹¹ Thomsen, *loc. cit.*

The following table gives the volume of gas, corrected to N.T.P., which can be absorbed by one cubic centimetre of water under a hydrogen sulphide pressure of 760 mm. : ¹

° C.	Absorption Coefficient.	° C.	Absorption Coefficient.	° C.	Absorption Coefficient.
0	4.621	25	2.257	70	1.010
5	3.935	30	2.014	80	0.906
10	3.362	40	1.642	90	0.835
15	2.913	50	1.376	100	0.800
20	2.554	60	1.176		

It will be seen that the solubility decreases rapidly as the temperature is raised, and this is still more evident in the following table, in which the solubility (volume of gas, corrected to N.T.P., absorbed by one volume of water at 760 mm. pressure) at various temperatures is given (the figures are somewhat less accurate than the foregoing). For the purpose of comparison analogous figures are given for alcohol, in which hydrogen sulphide is more soluble : ²

° C.	Solubility.	
	In Water.	In Alcohol.
0	4.37	17.89
5	3.97	14.78
10	3.59	11.99
15	3.23	9.54
20	2.91	7.42
25	2.61	5.62
30	2.33	..
35	2.08	..
40	1.86	..

The gas was first liquefied in 1823 by M. Faraday, who, twenty-two years later, successfully reduced the temperature by means of a mixture of solid carbon dioxide and ether to such a degree that the substance solidified.³ In Faraday's method, using an inverted U-tube, liquid hydrogen sulphide is obtained by placing in one limb materials such as hydrogen polysulphide or charcoal⁴ saturated with hydrogen sulphide,

¹ Winkler, *Zeitsch. physikal. Chem.*, 1906, 55, 350 ; Landolt and Bornstein, "Tabellen," 4th ed., pp. 597, 601.

² Carius, *Annalen*, 1855, 94, 140 ; Fauser, *Math. naturw. Ber. aus Ungarn.*, 1888, 6, 154.

³ Faraday, *Phil. Trans.*, 1823, 113, 160, 189 ; 1845, 135, 1, 170 ; *Annalen*, 1845, 56, 156. A modern adaptation of this method is described by Quam, *J. Amer. Chem. Soc.*, 1925, 47, 103.

⁴ Melsens, *Phil. Mag.*, 1873, [iv.], 46, 410.

from which the necessary hydrogen sulphide is liberated by gently warming; alternatively, the material enclosed in the one arm of the tube may be ferrous sulphide and concentrated hydrochloric acid, from which the hydrogen sulphide is obtained by subsequent interaction. If the empty arm of the inverted U-tube is then sufficiently cooled, the gas liquefies there under its own pressure. At the present day, however, on account of the ease with which low temperatures are obtainable, the liquefaction and solidification of hydrogen sulphide present no difficulties, passage of the gas into a tube cooled externally by liquid air being sufficient to produce the solid.

On elimination of sulphur from hydrogen sulphide an equal volume of hydrogen remains, which of course is evidence for the composition represented by the formula H_2S . Vapour density determinations also show that the gas consists of single H_2S molecules,¹ a value 34.085² having been obtained for the molecular weight, after making due corrections to the vapour density result. In the liquid state also there appears to be no association of the molecules and the molecular formula is still H_2S .

Liquid hydrogen sulphide is a colourless, very mobile fluid, which resembles the dry gas in being neutral to litmus.³ Its vapour pressure increases rapidly with rise of temperature, finally attaining a critical pressure of 88.9 atmospheres at the critical temperature, 100.4° C.⁴

Temperature .	0°	18.2°	50°	100° C.
Vapour pressure .	10.25	16.95	35.56	88.7 atmospheres. ⁵

At its ordinary boiling-point, -60.2° C. (760 mm.),⁶ the density of the liquid is 0.964. The solidified substance forms a crystalline, snow-like mass, m.pt. -83° C., of greater density than the liquid. The liquid is more highly refractive than water ($n_D = 1.384$ at 18.5° C.);⁷ the surface tension at -60° C. is 25.43 dynes per cm., and the dielectric constant 10.2 (air=1).⁸

In the liquid state, as in the gaseous condition, hydrogen sulphide consists of simple H_2S molecules. Like water, it is practically a non-conductor of electricity, its specific conductivity at about -80° C. being 1×10^{-11} mho;⁹ it is a good solvent for many substances; it dissolves sulphur without combining with it; hydrogen chloride and hydrogen bromide yield solutions in hydrogen sulphide which, in contrast to their aqueous solutions, are non-conducting. Ammonium chloride also yields a non-conducting solution, but alkylamine hydrochlorides,

¹ For a calculation of the actual molecular magnitude, see Exner, *Monatsh.*, 1885, 6, 249.

² Baume and Perrot, *J. Chim. phys.*, 1908, 6, 610.

³ Antony and Magri, *Gazzetta*, 1905, 35, 1, 206.

⁴ Dewar, *Phil. Mag.*, 1884, [v.], 18, 210; Leduc and Sacerdote, *Ann. Chim. Phys.*, 1898, [vii.], 15, 40; Ladenburg and Krugel, *Ber.*, 1900, 33, 637; de Forcrand and Fonzees-Diacon, *Compt. rend.*, 1902, 134, 281; Cardoso and Arni, *J. Chim. phys.*, 1912, 10, 504; Cardoso, *Gazzetta*, 1921, 51, 1, 153.

⁵ Olszewski, *Bull. Acad. Sci. Cracow*, 1890, 57.

⁶ For summaries of the physical properties of liquid hydrogen sulphide, see Cardoso and Arni, *loc. cit.*; Magri, *Atti R. Accad. Lincei*, 1907, [v.], 16, 518; McIntosh and Steele, *Proc. Roy. Soc.*, 1904, 73, 450, 454. For the heat of vaporisation, see Elliott and McIntosh, *J. Physical Chem.*, 1908, 12, 163.

⁷ Dechant, *Monatsh.*, 1884, 5, 615; Bleekrode, *Proc. Roy. Soc.*, 1884, 37, 339.

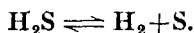
⁸ Magri, *loc. cit.*

⁹ Ralston and Wilkinson, *J. Amer. Chem. Soc.*, 1928, 50, 258.

however, yield solutions which do conduct electricity,¹ as also do certain organic ammonium salts, certain alkaloids and a number of oxygen compounds. The behaviour of such solutions is not analogous to that of aqueous solutions of ordinary electrolytes, since the conductivity increases enormously when the concentration is increased, and is, therefore, probably due to the formation, between solute and solvent, of some additive compound of conducting power.² The halides of phosphorus, arsenic and antimony dissolve in liquid hydrogen sulphide, and their solutions are electrically conducting, the conductivity considerably increasing with the atomic weight of the element.³

Iodine dissolves in liquid hydrogen sulphide without appreciable chemical change, the product being a deep red solution; bromine, however, is attacked vigorously, with formation of sulphur bromide.⁴ Hydrogen chloride also dissolves to a considerable extent without reaction, as also do some of the halides, although there is a tendency (*e.g.* with the chlorides of Hg, Hg⁺, Ag and Cu) to "thiohydrolysis," sulphide and hydrosulphide being formed.⁵ With the halides, in general, solubility and tendency to reaction increase as the basicity of the positive radical decreases.⁶ Liquid hydrogen sulphide reacts vigorously with dry liquid sulphur dioxide,⁷ and more slowly with selenium dioxide, forming selenium, sulphur and water. Oxidising agents cause separation of sulphur. Commercial iron and copper, even after prolonged immersion,⁸ are not affected by liquid hydrogen sulphide, which may therefore be stored in containers made of these metals.

Chemical Properties.—As has already been indicated (p. 48), hydrogen sulphide exhibits dissociation when heated above a certain temperature. The effect becomes appreciable near 400° C., and with rise in temperature the equilibrium mixture steadily contains less hydrogen sulphide until when near 1350° C. 50 per cent., and at 1700° C. approximately 75 per cent., is in the form of the free elements.⁹ A silent electric discharge through the gas hastens the decomposition,¹⁰ as also does the radiation from radium or radium emanation.¹¹ Heating the gas by a series of electric sparks naturally induces a similar dissociation, and, as the products diffuse from the path of the sparks into a cooler region, the sulphur gradually deposits in the solid condition, so that the gas undergoes a slow but finally complete decomposition, leaving an equal volume of hydrogen :¹²



¹ Quam and Wilkinson, *Proc. Iowa Acad. Sci.*, 1925, 32, 324.

² McIntosh and Steele, *loc. cit.*; McIntosh and Archibald, *Trans. Chem. Soc.*, 1904, 85, 1098.

³ Quam and Wilkinson, *loc. cit.*

⁴ Magri, *loc. cit.*; Antony and Magri, *loc. cit.*

⁵ Ralston and Wilkinson, *loc. cit.*

⁶ Quam, *J. Amer. Chem. Soc.*, 1925, 47, 103.

⁷ Quam, *loc. cit.*; *cf.* Magri, *loc. cit.*; Antony and Magri, *loc. cit.*

⁸ Fournier and Fritsch-Lang, *Compt. rend.*, 1927, 184, 1174.

⁹ Preuner, *Zeitsch. anorg. Chem.*, 1907, 55, 279; Preuner and Schupp, *Zeitsch. physikal. Chem.*, 1909, 68, 157.

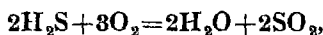
¹⁰ Berthelot, *Compt. rend.*, 1876, 82, 1360.

¹¹ Wourtsel, *Compt. rend.*, 1913, 157, 929.

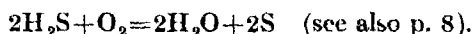
¹² See also Cluzel, *Ann. Chim. Phys.*, 1843, 84, 166; Myers, *Annalen*, 1871, 159, 124; Ber., 1872, 5, 259; Pélabon, *Compt. rend.*, 1897, 124, 35, 686; Beketoff, *Ber.*, 1871, 4, 933; Langer and Meyer, *ibid.*, 1895, 18, 135.

Contact with a heated platinum filament also promotes the decomposition.¹

The gas will not support the combustion of substances which are commonly termed combustible, but will itself burn readily in air or in oxygen, with a blue flame. In the presence of a relatively plentiful supply of air or oxygen, a condition easily obtained by burning the gas at a very fine jet, the products of combustion are water and sulphur dioxide :



but unless care is taken to ensure an excess of oxygen, the combustion is generally incomplete,² the foregoing products being accompanied by sulphur, which is produced according to the equation :



A mixture of hydrogen sulphide and oxygen explodes on the application of a flame, no free sulphur being formed if the proportion of oxygen is equal to or in excess of that required by the first of the two foregoing equations. In a closed vessel, an undried mixture of hydrogen sulphide with a termolecular proportion of oxygen will explode on being heated to 250° C.³ The heat of combustion of hydrogen sulphide to water and gaseous sulphur dioxide is 13.67 Cals. per gram-molecule.⁴

The bluish-violet layer observed against the glass surface of a flask when the latter is depressed on the upper part of a Bunsen flame appears to be due to the presence of hydrogen sulphide in the coal gas.⁵

As might be expected, slow flameless combustion of hydrogen sulphide is possible, and the process can be accelerated by contact with certain heated solids, *e.g.* charcoal, iron oxide, pumice or finely divided platinum or palladium.⁶ It is interesting that a catalytic effect of this type was applied to the recovery of sulphur from the "alkali waste" of the Leblanc soda process, so that an otherwise troublesome and unpleasant waste product was not only deprived of its nuisance-creating characteristics, but concurrently made to yield sulphur of a good quality.⁷ In the Chance-Claus process the hydrogen sulphide mixed with air was passed through a heated porous mass of iron oxide (bog iron ore) supported on fragments of firebrick. A process applicable to the removal of hydrogen sulphide from crude coal gas employs activated charcoal in a similar manner; in this case the gases can be passed through the material at a high velocity and emerge from the filters completely free from hydrogen sulphide,⁸ whilst pure sulphur results from the oxidation.

Dry hydrogen sulphide is stable in the air at ordinary temperatures, but when moist it undergoes oxidation,⁹ the rate being especially

¹ Taylor and Pickett, *J. Physical Chem.*, 1927, 31, 1212.

² Pedler, *Trans. Chem. Soc.*, 1890, 57, 625.

³ Freyer and Meyer, *Zeitsch. physikal. Chem.*, 1893, 11, 31.

⁴ Thomsen, *Thermochemische Untersuchungen*, 1882.

⁵ Johansen, *Zeitsch. wiss. Photochem.*, 1912, 11, 20. For measurements of flame speeds of H₂S-air mixtures burnt in a horizontal tube, see Chamberlin and Clarke, *Ind. Eng. Chem.*, 1928, 20, 1016.

⁶ Piria, *Ann. Chim. Phys.*, 1840, 74, 331.

⁷ See Lunge, *Sulphuric Acid and Alkali*, 3rd ed. (1909), vol. II., pp. 945 *et seq.* (Gurney and Jackson); Lunge and Cumming, *Manufacture of Acids and Alkalis* (1923), vol. I., p. 142 (Gurney and Jackson).

⁸ See K. Evans, Pearson and Reusemann, *Chem. Trade J.*, 1929, 85, 568.

⁹ Dumas, *Ann. Chim. Phys.*, 1846, [iii.], 18, 502; Deville, *Compt. rend.*, 1852, 35, 261.

appreciable if the temperature is raised a little, *e.g.* to 70°–80° C. Aqueous solutions of the gas undergo a similar atmospheric oxidation, causing the well-known deposit of sulphur in "hydrogen sulphide water," and at the same time acquire traces of sulphuric acid.¹ Exposure to light facilitates oxidation of both gas and solution. In solution oxidation is accelerated by the presence of finely divided nickel.²

For the preservation of hydrogen sulphide solutions a covering layer of paraffin oil or the addition of such substances as sugar, glycerol or salicylic acid has been suggested;³ in the case of the latter substances it is possible that their "negative catalytic effect" may be due to their rendering inactive traces of some otherwise powerful catalyst (compare p. 124).

On account of its tendency to oxidation, hydrogen sulphide is frequently employed as a reducing agent in organic chemistry. In the case of solutions in *N*-hydrochloric acid the oxidation is catalytically accelerated by a mixture of manganese and iron.⁴

With oxidising agents other than free oxygen, hydrogen sulphide yields sulphur or sulphuric acid, according to the conditions. Concentrated sulphuric acid oxidises the gas to free sulphur (see also p. 170), being itself reduced to sulphur dioxide;⁵ sulphur dioxide also effects oxidation to sulphur (see p. 115); hydrogen peroxide solution causes gradual oxidation to sulphur, but in the presence of alkalis oxidation proceeds further, to the formation of sulphate.⁶

If the gas is passed over sodium peroxide, a violent reaction occurs both in the presence and the absence of air. If the peroxide is previously heated, the reaction is accompanied by flame, and if excess of air is present a loud detonation is produced. In the absence of air the products consist of sulphide and polysulphide of sodium, together with a small amount of thiosulphate and sulphate; in the presence of air very little sulphide is formed, sodium sulphate and free sulphur being obtained.⁷

Ozone causes partial conversion of aqueous hydrogen sulphide to sulphuric acid, sulphur being simultaneously produced.⁸ With nitric acid the oxidation is very vigorous and with the fuming acid may be explosive, the product being sulphuric acid;⁹ hydrogen sulphide will burn in nitric acid vapour.¹⁰ The fact that carbon dioxide appears to liberate sulphur from hydrogen sulphide at a red heat may not be due to direct oxidation but to previous thermal dissociation into sulphur and hydrogen, the latter subsequently being converted into water, whilst the carbon dioxide is reduced to monoxide.¹¹ Hydrogen sulphide reacts with nitric oxide to form sulphur, nitrogen and water, especially

¹ Vauquelin, *J. Pharm. Chim.*, 1825, 11, 126; Filhol, *Ann. Chim. Phys.*, 1873, [iv.], 28, 529.

² Krebs, *Biochem. Zetsch.*, 1929, 204, 343.

³ Lepage, *J. Pharm. Chim.*, 1867, [iv.], 5, 256; Mohr, *Zetsch. Chem.*, 1862, 8, 113; Shilton, *Chem. News*, 1889, 60, 235.

⁴ Krebs, *loc. cit.*

⁵ Geuther, *Annalen*, 1858, 109, 71.

⁶ Classen and Bauer, *Chem. News*, 1883, 47, 288; *Ber.* 1883, 16, 1062.

⁷ Zenghelis and Horsch, *Compt. rend.*, 1916, 163, 17, 440.

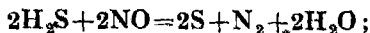
⁸ Bresciani, *Ann. Chim. Applicata*, 1915, 4, 343.

⁹ Kessel, *Ber.*, 1879, 12, 2305; Kemper, *Annalen*, 1857, 102, 342.

¹⁰ Austen, *Amer. Chem. J.*, 1889, 11, 172; *Chem. News*, 1899, 59, 208.

¹¹ Köhler, *Ber.*, 1878, 11, 205; Meyer and Schuster, *ibid.*, 1911, 44, 1931; Gautier, *Compt. rend.*, 1906, 143, 7; Costeanu, *ibid.*, 1913, 156, 1985.

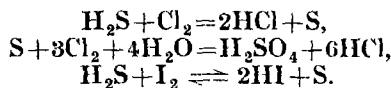
in the presence of catalysts such as silica gel (alone or impregnated with ferric oxide) or glass wool :



no trace of nitrous oxide or ammonium sulphide is formed.¹ The reaction, however, appears to be more complex than is indicated in the equation, and it has been suggested that the nitric oxide first forms condensed molecules, N_2O_2 , which are adsorbed by the catalyst and bring about the oxidation. With nitrous acid solution, hydrogen sulphide produces nitric and nitrous oxides when the nitrous acid is in excess, but ammonia and hydroxylamine when the hydrogen sulphide is in excess ;² free sulphur and even a little sulphuric acid are produced.

Aqueous solutions of alkali chromates yield with hydrogen sulphide a precipitate of chromium hydroxide contaminated with sulphur, whilst alkali sulphide, polysulphide, thiosulphate and colloidal sulphur remain in the solution.³

Chlorine and bromine liberate sulphur from gaseous hydrogen sulphide, the reaction being capable of going further in aqueous solution, because under these conditions the sulphur may be oxidised to sulphuric acid.⁴ With iodine, appreciable reaction occurs only in aqueous solution, and even then the chemical change may not be complete, ceasing when the hydriodic acid attains a concentration of approximately 25 per cent. in the solution. Fluorine attacks gaseous hydrogen sulphide so violently as to cause spontaneous inflammation.⁵



Under considerably increased pressure, or when strongly cooled, hydrogen sulphide and water can combine to form a crystalline compound of which the composition is probably $\text{H}_2\text{S} \cdot 6\text{H}_2\text{O}$; if the temperature and pressure are allowed to revert to the normal conditions, the crystals at once dissociate into the constituent substances.⁶ An additive compound of methyl ether and hydrogen sulphide, $(\text{CH}_3)_2\text{O} \cdot \text{H}_2\text{S}$, melting at -148.5°C ., is also capable of existence at low temperatures ;⁷ although the nature of this compound may be allied to that of the additive compound with water, it appears more probable that the methyl ether compound is an oxonium salt.

Hydrogen sulphide appears to be able to play, in a feeble manner, a rôle analogous to that of water in compounds containing so-called

¹ Pierce, *J. Physical Chem.*, 1929, 33, 22.

² Bagster, *J. Chem. Soc.*, 1928, p. 2631 ; Divers, *Trans. Chem. Soc.*, 1887, 51, 48.

³ Dunncliff and Soni, *J. Physical Chem.*, 1929, 33, 81.

⁴ Rose, *Ann. Phys. Chem.*, 1839, [ii.], 47, 161 ; Naumann, *Ber.*, 1876, 9, 1574 ; Berthelot, *Compt. rend.*, 1873, 76, 746 ; 1878, 87, 667.

⁵ Moissan, *Ann. Chim. Phys.*, 1891, [vi.], 24, 224. For an account of the action of iodine trichloride on hydrogen sulphide, see MacIvor, *Chem. News*, 1902, 86, 5 ; and of iodine acid in the presence of hydrochloric acid, see Dean, *J. Amer. Chem. Soc.*, 1915, 37, 1134.

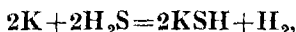
⁶ Wöhler, *Annalen*, 1840, 33, 125 ; 1853, 85, 376 ; de Forcrand, *Compt. rend.*, 1882, 94, 967 ; 1888, 106, 849, 939, 1357 ; 1902, 124, 281 ; 125, 959, 1344 ; Cailletet and Bordet, *ibid.*, 1882, 95, 60 ; Scheffer and Meijer, *Verslag. Akad. Wetensch. Amsterdam*, 1919, 27, 1104 ; Quam, *J. Amer. Chem. Soc.*, 1925, 47, 103 ; Scheffer, *Proc. K. Akad. Wetensch. Amsterdam*, 1911, 13, 829 ; 14, 195.

⁷ Baume and Perrot, *Compt. rend.*, 1911, 152, 1763.

"water of crystallisation"; thus, aluminium bromide in a fused condition or dissolved in carbon disulphide absorbs gaseous hydrogen sulphide with formation of a colourless crystalline compound, $\text{AlBr}_3 \cdot \text{H}_2\text{S}$, which melts at 83°C . and is decomposed by water with liberation of hydrogen sulphide.¹ Boron trichloride reacts with liquid hydrogen sulphide, forming² white crystals of composition $\text{BCl}_3 \cdot 12\text{H}_2\text{S}$.

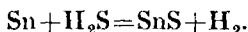
Hydrogen Sulphide as an Acid.—In the anhydrous condition, whether as gas or liquid, hydrogen sulphide has no acidic properties. When moist or in aqueous solution, however, it behaves as a feeble acid, whence the occasional name "hydrosulphuric acid." For the characteristic test with lead acetate paper or for the reddening of litmus paper, the presence of at least a little moisture is essential.³

With ammonia, the gas combines to form ammonium sulphide or ammonium hydrosulphide, according to the relative quantities of the reagents.⁴ The alkaloids, which may be regarded as organic derivatives of ammonia, also combine with hydrogen sulphide, forming crystalline salts; such salts of cinchonine, quinine, strychnine, brucine and nicotine have been known for many years.⁵ When heated in the gas, the alkali metals yield the acid sulphides:

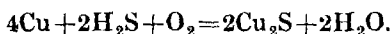


which can also be obtained by the action of excess of the gas on solutions of the hydroxides,⁶ or of the metals in absolute alcohol.⁷

Tin, when heated in the gas, undergoes conversion into stannous sulphide without the gaseous volume being permanently altered thereby:



Many other metals yield sulphides if treated with gaseous hydrogen sulphide under suitable conditions;⁸ thus mercury, silver and copper fail to react with dry hydrogen sulphide,⁹ but if the gas be moist, and especially if oxygen or air also be present, the metals react readily, with formation of the corresponding sulphide, whilst in the presence of oxygen the hydrogen is oxidised to water;¹⁰ the reaction for copper is represented by the equation:



Boron and silicon likewise decompose hydrogen sulphide at high temperatures, liberating hydrogen and forming sulphides.¹¹

The oxides of many metals, if heated in a stream of the gas, become

¹ Plotnikov, *J. Russ. Phys. Chem. Soc.*, 1913, 45, 1162.

² Ralston and Wilkinson, *J. Amer. Chem. Soc.*, 1928, 50, 258.

³ Hughes, *Phil. Mag.*, 1892, [v.], 33, 471.

⁴ Magnusson, *J. Physical Chem.*, 1907, 11, 21; Thomas and Riding, *J. Chem. Soc.*, 1923, 123, 1181.

⁵ Schmidt, *Bull. Soc. chim.*, 1876, 26, 218.

⁶ de Forcrand, *Compt. rend.*, 1899, 128, 1519, Thomsen, *Ber.*, 1870, 3, 192; 1872, 5, 233; Kolbe, *J. prakt. Chem.*, 1871, [ii.], 4, 412.

⁷ Rule, *Trans. Chem. Soc.*, 1911, 99, 558.

⁸ See Jellinek and Zakowski (*Zeitsch. anorg. Chem.*, 1925, 142, 1) on the affinity of the metals for sulphur, and investigation of the equilibrium $\text{MS} + \text{H}_2 \rightleftharpoons \text{M} + \text{H}_2\text{S}$.

⁹ Hughes, *loc. cit.*; Cardoso and Arni, *J. Chem. phys.*, 1912, 10, 504.

¹⁰ Merz and Weith, *Zeitsch. Chem.*, 1869, 12, 241; Berthelot, *Ber.*, 1879, 12, 397; *Compt. rend.*, 1879, 89, 684.

¹¹ Sabatier, *Bull. Soc. chim.*, 1882, [ii.], 38, 153; Lorenz, *Ber.*, 1891, 24, 1501.

converted into the corresponding sulphides, sometimes with simultaneous formation of sulphur dioxide if the reaction becomes vigorous.¹ With peroxides and dioxides the heat of the reaction may be so great as to cause the mass to become incandescent.²

Metallic hydroxides, on account of their more decidedly alkaline character, generally react more readily than the corresponding oxides,³ and a mixture of soda-lime, if submitted to the action of a current of hydrogen sulphide mixed with air, becomes white hot.⁴

On account of the feeble acidity of hydrogen sulphide, the alkali carbonates in aqueous solution are decomposed only as far as the hydrogen carbonates, an equilibrium being attained :⁵



In agreement with the relative reactivities of the alkali hydroxides and carbonates towards hydrogen sulphide, it has been observed that the blackening of basic lead carbonate by the gas is due to the conversion into sulphide of the lead hydroxide only and not of the carbonate.⁶

An aqueous solution of hydrogen sulphide is only feebly acidic, the dissolved substance being only partly ionised ; the ions present consist almost entirely of H^+ and SH^+ , from the dissociation :



and very few S^{2-} ions are present as a result of further dissociation of the hydrosulphide ion.⁷

Physiological Action.—If breathed into the lungs hydrogen sulphide has an exceedingly poisonous action, air containing as little as 0.1 per cent. being capable in time of producing a fatal effect.⁸ Its action is believed to be due to the formation of sodium sulphide in the blood, which then affects the nerve centres.⁹ In considerably more dilute condition than 0.1 per cent. it will produce sickness and headache.¹⁰ Poisoning by absorption of the gas through the skin or mucous membrane is apparently not possible.¹¹ On account of the harmful action of the gas, many devices¹² have been suggested for the precipitation of sulphides in analytical processes without liberating the hydrogen

¹ Schumann, *Annalen*, 1877, 187, 286 ; Bottger, *J. prakt. Chem.*, 1867, 103, 308 ; Thomsen, *ibid.*, 1879, [ii.], 19, 17 ; Berthelot, *Compt. rend.*, 1874, 78, 1176 ; Gautier, *Compt. rend.*, 1906, 143, 7.

² Bottger, *loc. cit.* ; Zenghelis and Horsch, *Compt. rend.*, 1916, 163, 440.

³ Kirscher, *Annalen*, 1839, 31, 339.

⁴ Guareschi, *Atti R. Accad. Sci. Torino*, 1916, 51, 4, 59, 372, 951.

⁵ Berl and Rittener, *Zeitsch. angew. Chem.*, 1907, 20, 1637.

⁶ Sacher, *Chem. Zeit.*, 1910, 34, 647.

⁷ Prytz, *Ann. Phys. Chem.*, 1882, [iii.], 17, 875 ; Ostwald, *J. prakt. Chem.*, 1885, [ii.], 32, 307 ; Smith, *J. Amer. Chem. Soc.*, 1922, 44, 1500.

⁸ Lehmann, *Ber.*, 1888, 21, 67 ; *Arch. Hygiene*, 1892, 14, 135 ; Wilson, *Amer. J. Pharm.*, 1894, 65, 12 ; *Chem. News*, 1894, 69, 159.

⁹ Uchinsky, *Zeitsch. physiol. Chem.*, 1892, 17, 220 ; Pohl, *Ber.*, 1887, 20, 595 ; Plyron, *ibid.*, 1887, 20, 295.

¹⁰ Habermann, Kulka and Homma, *Zeitsch. anal. Chem.*, 1911, 50, 1.

¹¹ Chauveau and Tissot, *Compt. rend.*, 1901, 133, 137.

¹² See, for example, Donath, *Chem. Zeit.*, 1908, 32, 629 ; Alvarez, *Anal. Soc. Quim. Argentina*, 1913, 1, 122, 223 ; Orlovsky, *Ber.*, 1883, 16, 807 ; Schiff and Tarugi, *ibid.*, 1894, 27, 3437 ; Bayer, *Pharm. Post*, 1918, 354 ; Schweitz, *Apoth. Ztg.*, 1919, 57, 140 ; Vortmann, *Boll. Sci. tecn.*, 3, No. 5 ; *Giorn. Chim. Ind. Appl.*, 1921, 3, 565.

sulphide in the gaseous condition, for example, the use of an alkali sulphide.

The Metallic Sulphides.

Formation.—Various methods are available for the preparation of the sulphides of the metals; only a few of the more general are here mentioned, details of other methods being obtainable under the headings of the respective metals in other volumes of this series.

(a) Direct combination of the metal and sulphur can generally be effected,¹ sometimes even at the ordinary temperature. This process is of especial advantage for the preparation of sulphides which are decomposed by water, *e.g.* aluminium sulphide (see also p. 38). Finely divided mixtures of zinc and sulphur may be exploded by shock, heat or friction.²

(b) The metal may be heated in a current of hydrogen sulphide gas. As a rule this method will have the disadvantage relative to method (a) that the necessity to effect the displacement of hydrogen will render the reaction more difficult, especially with the less electro-positive metals.

(c) The metallic oxide, either alone or mixed with charcoal, may be heated in a stream of carbon disulphide vapour or merely with carbon disulphide under pressure, *e.g.* at 250° C. This process shares with method (a) the advantage of being conveniently applicable to the production of sulphides which are decomposed by water.

(d) Salts of the metal with one of the sulphur oxyacids, *e.g.* a sulphate, sulphite or thiosulphate, may be reduced to the corresponding sulphide by heating with some suitable reducing agent such as charcoal, hydrogen or sulphur.³ This method is commonly employed as a stage in the conversion of the mineral barium sulphate into other barium salts, reduction with charcoal first yielding the more reactive sulphide.⁴

(e) In the case of many metals the sulphides can be formed by precipitation from aqueous salt solutions.⁵ The extensive use of hydrogen sulphide as a reagent in qualitative analysis depends, of course, on the different conditions necessary for the formation of the various sulphides. Some sulphides, *e.g.* antimony sulphide, can be quantitatively precipitated from solutions which are fairly strongly acidic, whereas in other cases the presence of acid leads to the setting up of an equilibrium; ⁶ thus, lead sulphide is precipitated only partially in a

¹ Franck, *Bull. Soc. chim.*, 1897, [iii], 17, 504; Spring, *Ber.*, 1883, 16, 999; 1884, 17, 1218; Schwarz, *ibid.*, 1882, 15, 2505; Fonzes-Diacon, *Compt. rend.*, 1900, 130, 1314; Thomsen, *J. prakt. Chem.*, 1879, [ii], 19, 11; Schumann, *Annalen*, 1877, 187, 286; Orłowski, *J. Russ. Phys. Chem. Soc.*, 1881, 1, 547; *Ber.*, 1881, 14, 2823; Schürmann, *Annalen*, 1888, 249, 326; *Ber.*, 1889, 22, 129; Danneel and Fröhlich, *Zeitsch. angew. Chem.*, 1927, 40, 809.

² Coustal and Prevet, *Compt. rend.*, 1929, 188, 703; Prevet, *ibid.*, p. 903.

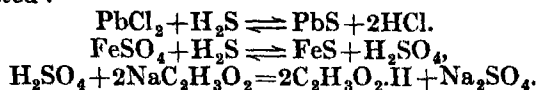
³ de Koninck, *Ber.*, 1887, 20, 397. See also Budnikov and Shilov, *J. Soc. Chem. Ind.*, 1928, 47, 111 T; Bassett, *American Patent*, 1722170 (1929); *British Chem. Abs.*, 1929, B, 813.

⁴ See under Barium, this series, Vol. III., Part I., 1925, p. 224.

⁵ Cooke, *Chem. News*, 1873, 28, 64; Delfs, *Ber.*, 1879, 12, 2182; Dede and Bonin, *ibid.*, 1922, 55, [B], 2327. See also Hackl, *Chem. Zeit.*, 1924, 48, 326; Piccard and Thomas, *Helv. Chim. Acta*, 1923, 6, 1046.

⁶ Berthelot, *Compt. rend.*, 1874, 78, 1178, 1247; Linder and Picton, *Chem. News*, 1890, 61, 200; *Trans. Chem. Soc.*, 1892, 61, 114; Bruner and Zawadzki, *Bull. Acad. Sci. Cracow*, 1909, 267.

solution containing 5 per cent. of hydrogen chloride, whilst ferrous sulphate solution yields ferrous sulphide only in the presence of sodium acetate or ammonium acetate, which removes the sulphuric acid as fast as it is liberated :

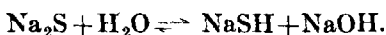


The presence of alkali and alkaline earth chlorides may also hinder precipitation of the sulphide; thus, from a 0.001 molar solution of lead chloride in water at 20° C., precipitation is completely inhibited by hydrogen chloride alone if in a concentration of 1.4*N*, and by decreasing concentrations of the acid in the presence of increasing quantities of calcium, ammonium or potassium chloride. Cadmium sulphide, precipitated from hydrochloric acid solution, contains adsorbed chlorine,¹ the amount depending on the conditions of the precipitation; the precipitation is incomplete at 80° C.

By using alcoholic benzene solutions of the alkali alcoholates it has been found possible to precipitate the corresponding alkali hydrogen sulphides by hydrogen sulphide.²

(*f*) Electrolysis of a solution of an alkali sulphide with an anode consisting of a metal such as copper, cadmium or silver will lead to the conversion of the anodic metal into sulphide.³

Properties.—In aqueous solution the normal sulphides of the alkali metals are very largely hydrolysed into the corresponding hydro-sulphides, so that the solutions react strongly alkaline on account of the liberated alkali hydroxide :⁴



Electrolysis of such solutions with platinum electrodes and with low current densities yields polysulphides; with higher current densities sulphates and dithionates are formed.⁵

The solutions undergo oxidation on exposure to air, sulphur first being liberated and then polysulphides formed, which in turn are oxidised to thiosulphates. The rate of this oxidation is greatly accelerated by the presence of small quantities of certain of the heavy metals, particularly manganese and nickel.⁶

Solutions of the alkali sulphides give a deep violet to purple coloration with a solution of sodium nitroprusside, and as mentioned on p. 43, this may be used as a test for sulphides. By the interaction of the nitroprusside with the sulphides of lithium, sodium, potassium and rubidium, stable crystalline compounds of the type $\text{M}_4[\text{Fe}(\text{CN})_5\text{NOS}]$ have been obtained. From electrotitrimetric evidence the reaction appears to proceed in two stages :⁷

¹ Weiser and Durham, *J. Physical Chem.*, 1928, 32, 1061; cf. Egerton and Raleigh, *Trans. Chem. Soc.*, 1923, 123, 3019.

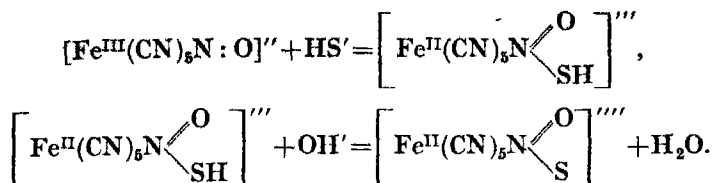
² Rule, *Trans. Chem. Soc.*, 1911, 99, 558; 1913, 103, 871.

³ Lorenz, *Zeitsch. anorg. Chem.*, 1896, 12, 442. For an electrolytic method for anti-monny sulphide, see Tocco, *Gazzetta*, 1924, 54, 23.

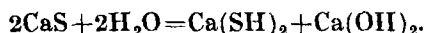
⁴ de Clermont and Frommel, *Compt. rend.*, 1878, 86, 828; 87, 330; *Ann. Chim. Phys.*, 1879, [v.], 18, 189; Béchamp, *Compt. rend.*, 1868, 67, 825; Knox, *Zeitsch. Elektrochem.*, 1906, 12, 477.

⁵ Krebs, *Biochem. Zeitsch.*, 1929, 204, 343.

⁷ Scagliarini and Pratesi, *Atti R. Accad. Lincei*, 1928, [vi.], 8, 75.



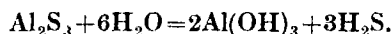
All the other normal sulphides are insoluble in water or are decomposed by it. The sulphides of the alkaline earth metals are sparingly soluble but, like the alkali sulphides, undergo hydrolysis to the corresponding hydrosulphides :



These hydrosulphides of the alkaline earth metals are soluble in water and therefore, by treating an emulsion of the normal sulphides with a current of hydrogen sulphide, it is possible to obtain solutions of the hydrosulphides ¹ $\text{Ca}(\text{SH})_2$, $\text{Sr}(\text{SH})_2$, $\text{Ba}(\text{SH})_2$ and $\text{Mg}(\text{SH})_2$.

A remarkable property of the sulphides of the alkaline earth metals and of beryllium and zinc is their power, when certain impurities are present, to exhibit phosphorescence after exposure to bright light. The phenomenon is not due to slow oxidation and is still observable in samples which have been kept hermetically sealed for years ; it is obvious, therefore, that the effect is a physical one and not analogous to the phosphorescence observable with sulphur (p. 37). The nature and amount of impurity present considerably affect the phosphorescence, chlorides for example causing an increase ; some impurities inhibit the action.²

The sulphides of aluminium and silicon are decomposed immediately by water at the ordinary temperature, whilst even the sulphides of the heavier metals such as copper, lead and iron are decomposed by steam at a red heat ³ (see also p. 50) :



Some sulphides, such as lead sulphide or iron pyrites, which are not decomposed by hydrochloric acid alone, yield their sulphur as hydrogen sulphide when metallic zinc is also present, the nascent hydrogen effecting the desired result.⁴ Hydrogen sulphide is also formed when iron pyrites is heated with coal, or in a stream of dry or moist hydrogen or moist carbon dioxide.⁵

¹ Berthelot, *Compt. rend.*, 1871, 73, 1054. See also Lunder and Picton, *Trans. Chem. Soc.*, 1892, 61, 114 ; Riesenfeld and Feld, *Zeitsch. anorg. Chem.*, 1921, 116, 213.

² Le Roux, *Compt. rend.*, 1905, 140, 84, 239 ; Henry, *ibid.*, 1896, 122, 662 ; Lumière and Lumière, *ibid.*, 1899, 125, 549 ; Pictet, *ibid.*, 1894, 119, 527 ; Lenard, Onnes and Pauli, *Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 157 ; Vanino and others, *J. prakt. Chem.*, 1905, [ii.], 71, 196 ; 1906, [ii.], 73, 446 ; 1909, [ii.], 80, 69 ; Breteau, *Compt. rend.*, 1915, 161, 732 ; MacDougall, Stewart and Wright, *Trans. Chem. Soc.*, 1917, 111, 663 ; Thomaschek, *Ann. Physik*, 1921, [iv.], 65, 189 ; Lenard, *ibid.*, 1923, [iv.], 68, 553 ; Smith, *J. Amer. Chem. Soc.*, 1922, 44, 1500 ; Tiede and Richter, *Ber.*, 1922, 55, [B], 69 ; Tiede and Goldschmidt, *ibid.*, 1929, 62, [B], 758 ; Prevet, *Compt. rend.*, 1929, 188, 903 ; Coustal and Prevet, *ibid.*, p. 703.

³ Regnault, *Ann. Chim. Phys.*, 1836, 62, 374 ; Schumann, *Annalen*, 1877, 187, 286 ; Gautier, *Compt. rend.*, 1906, 142, 1465.

⁴ Casamajor, *Chem. News*, 1881, 44, 44 ; Skey, *Chem. News*, 1873, 27, 161.

⁵ Drakeley, *Trans. Chem. Soc.*, 1917, 111, 853.

Cobaltous, nickelous and zinc sulphides when spread on a lead plate and subjected to cathodic polarisation in aqueous sulphuric acid, suffer reduction, some of the metal passing into solution and hydrogen sulphide being liberated.¹

The sulphides of the heavier metals are characterised by their pronounced colours, insolubility and ability under certain conditions to carry down, when precipitated, normally soluble sulphides of other metals. The freshly precipitated sulphides differ somewhat in solubility from those which have "aged" for some time; they are also capable of forming double salts, such as $2\text{HgS} \cdot \text{HgCl}_2$, $\text{FeS} \cdot \text{NiS}$, $\text{Ti}_2\text{S}_3 \cdot 2\text{CuS}$. Cadmium and manganese sulphides, precipitated together by means of ammonium sulphide, yield the compound $2\text{MnS} \cdot 3\text{CdS}$. Mercuric sulphide, precipitated from acid solutions containing zinc or cadmium, always carries down considerable amounts of the latter metals, and the ordinary use of hydrogen sulphide in qualitative analysis fails to effect a complete separation of mercury from zinc and cadmium, or, for similar reasons, of tin from cobalt. Examples of solubility changes are as follows: nickel sulphide is insoluble in 10 per cent. hydrogen chloride solution, but when co-precipitated with lead sulphide it is appreciably soluble; manganese sulphide is readily soluble in acetic acid, but digestion with acetic acid of a co-precipitated mixture of manganese and zinc sulphides leaves a residue of zinc sulphide which may contain up to 24 per cent. of manganese.² The addition of a little hydrogen peroxide aids solution of mercuric sulphide in dilute hydrochloric acid, and of nickel and cobalt sulphides in dilute acetic acid.³

The stability of the sulphides other than those of the alkali metals, the alkaline earth metals and aluminium, ranges from that of manganese sulphide, which is easily decomposed by dilute acids and slowly by ordinary steam, to that of mercuric sulphide or molybdenum sulphide, which resist the action of concentrated hydrochloric acid solution.

It will be noticed that, as a general rule, the more basic the character of a metal the more stable is its sulphide towards oxidation; an analogy therefore appears to exist between the function of sulphur in a sulphide and oxygen in an oxide. This analogy extends, in a less marked manner, to the behaviour of the corresponding sulphides and oxides towards alkalis. Just as carbon dioxide, arsenious oxide and the antimony oxides lend themselves to salt formation with alkalis, so carbon disulphide, arsenious sulphide and the antimony sulphides can combine with the alkali sulphides, giving rise to sulphur compounds (*thio-salts*) of analogous composition.⁴ Indeed, on treatment with an alkali, such a sulphide generally produces a mixture of the corresponding oxy-salt and the thio-salt. These sulphides can therefore be regarded as "thio-anhydrides." From the similarity in behaviour, it is probable that the sulphides are structurally analogous to the corresponding oxides.

¹ Fischbeck and Einecke, *Zeitsch. anorg. Chem.*, 1928, 175, 341.

² Feigl, *Zeitsch. anal. Chem.*, 1924, 65, 25; Scheringa, *Pharm. Weekblad*, 1918, 55, 431. For the interaction of solid silver and cuprous sulphides with other solid salts, see Tubandt and Reinhold, *Zeitsch. physikal. Chem.*, 1929, 140, 291.

³ Komarovskiy, *Zeitsch. anal. Chem.*, 1927, 72, 293.

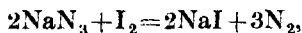
⁴ Rössing, *Zeitsch. anal. Chem.*, 1902, 41, 1; Stanek, *Zeitsch. anorg. Chem.*, 1898, 17, 117; Weinland and Rumpf, *Ber.*, 1896, 29, 1008; *Zeitsch. anorg. Chem.*, 1897, 14, 42; Moissan, *Compt. rend.*, 1880, 90, 817; McLauchlan, *Ber.*, 1901, 34, 2166. See also under the respective elements in other volumes of this series.

The sulphides of the heavy metals may readily be desulphurised by ignition with aluminium; ¹ even zinc sulphide, to which is attributed a higher heat of formation than to the equivalent amount of aluminium sulphide, may be thus reduced.¹

The crystal structures of certain metallic sulphides have been investigated.²

Detection and Estimation of Hydrogen Sulphide.

Even when only small quantities are present in a gaseous mixture or in aqueous solution, free hydrogen sulphide can be detected readily by its odour (a concentration of 1 in 700,000 is detectable), by its effect on paper moistened with lead acetate solution ³ and by the "methylene blue" reaction.⁴ The last test, by which it is possible to detect less than one milligramme of the substance in 40 litres of water, is applied by adding to the solution (obtained, if necessary, by bubbling the suspected gas through water) one-fiftieth of its volume of concentrated hydrochloric acid, a very little *p*-aminodimethylaniline sulphate, and then two or three drops of dilute ferric chloride solution; in the presence of hydrogen sulphide the liquid becomes coloured, from the formation of Methylene Blue, an organic dye containing sulphur.⁵ In the presence of alkali, hydrogen sulphide reacts with a dilute solution of sodium nitroprusside to give an intense purple coloration. In the presence of a sulphide (soluble or insoluble), sodium azide and iodine react in solution with vigorous evolution of nitrogen,⁶



and the reaction is claimed to be more sensitive as a test for sulphide than any of the tests already mentioned; thiosulphates, tri-, tetra- and penta-thionates also catalyse the reaction, however,⁷ but not dithionates, sulphites, selenides, tellurides, arsenides or antimonides, nor does free sulphur. The test is useful in detecting sulphides in minerals and hydrogen sulphide in natural waters. Other tests which are less satisfactory are based on the blackening of metallic silver and on the reduction of weak iodine solution (plus starch) or of potassium ferricyanide in the presence of ferric chloride; in the former case the blue colour of the solution is bleached, whilst in the latter the solution becomes coloured with Prussian Blue.

When present in considerable quantity in a gaseous mixture, hydrogen sulphide can be estimated by the increase in weight of suitable absorption tubes, containing, for example, moist granulated salts of lead or copper.⁸ More convenient, however, is the oxidation of the gas to sulphuric acid by passage through bromine water or other suitable

¹ Parravano and Agostini, *Gazzetta*, 1919, 49, i., 103.

² See Huggins, *Phys. Review*, 1923, 21, 211; Davey, *ibid.*, p. 213; Kolkmeijer, Bijvoet and Karssen, *Proc. K. Akad. Wetensch. Amsterdam*, 1924, 27, 390; *Rec. Trav. chim.*, 1924, 43, 894.

³ Schneider, *Zeitsch. anal. Chem.*, 1883, 22, 81; Wilmet, *Compt. rend.*, 1927, 184, 287.

⁴ Caro and Fischer, *Ber.*, 1883, 16, 2234; *Zeitsch. anal. Chem.*, 1884, 23, 226.

⁵ For the application of this reaction as a colorimetric method for the estimation of hydrogen sulphide, see Mecklenburg and Rosenkränzer, *Zeitsch. anorg. Chem.*, 1914, 86, 143; also Bach, *Gas- u. Wasserfach*, 1929, 72, 154.

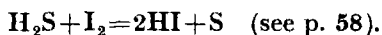
⁶ Feigl, *Zeitsch. anal. Chem.*, 1928, 74, 369.

⁷ Metz, *ibid.*, 1929, 76, 347.

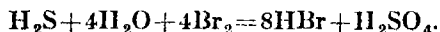
⁸ Fresenius, *ibid.*, 1871, 10, 75; Ludwig, *Annalen*, 1872, 162, 55.

oxidising agent, when the quantity of sulphuric acid may subsequently be determined either volumetrically or gravimetrically;¹ the same process obviously may be applied to aqueous solutions of hydrogen sulphide. Another type of method is based on the conversion of the hydrogen sulphide into some insoluble sulphide such as that of lead, copper or mercury, when the amount of metallic sulphide may be determined by oxidation of its sulphur to sulphuric acid;² if only traces of hydrogen sulphide are under examination, this type of method may be applied colorimetrically.

Hydrogen sulphide is sometimes estimated volumetrically by treating a solution containing less than 0.04 per cent. with excess of standard iodine and then after a short period titrating the residual iodine in the usual manner with sodium thiosulphate or arsenious oxide; accurate direct titration is not possible:³



A modification of this method is to effect the oxidation by a known quantity of bromine (obtained by the addition of standard potassium bromate solution together with potassium bromide and hydrochloric acid) and subsequently add excess of potassium iodide; the superfluous bromine liberates a corresponding amount of iodine, which can be estimated titrimetrically; hence the bromine consumed and the hydrogen sulphide oxidised can be calculated.⁴ The chemical change in this case is:



The sulphur in sulphides from which hydrogen sulphide can be liberated by acids can naturally be estimated by suitable application of the foregoing methods.⁵

An accurate electrometric method applicable to soluble sulphides consists in precipitating as silver sulphide in alkaline solution by titration with standard ammoniacal silver solution.⁶ The change of E.M.F. at the end-point is considerable. The method is satisfactory in the presence of sulphite, sulphate, thiosulphate, polysulphide or chloride.

¹ For example see Winkler, *Zeitsch. angew. Chem.*, 1916, 29, 1, 383; also Classen and Bauer, *Ber.*, 1883, 16, 1061; Eliasberg, *ibid.*, 1886, 19, 320.

² Classen and Bauer, *loc. cit.*; Lyte, *Compt. rend.*, 1856, 43, 765; Weil, *ibid.*, 1886, 102, 1487; *Ber.*, 1887, 20, 695; Friedheim, *ibid.*, 1887, 20, 59, 1483.

³ Brunck, *Zeitsch. anal. Chem.*, 1906, 45, 541; Jayson and Vesper, *J. Ind. Eng. Chem.*, 1917, 9, 975. For application of this method to sea-water, see Drucker, *Internat. Rev. Hydrobiol. Hydrogr.*, 1926, 16, 130; *Chem. Zentr.*, 1927, ii., 1189.

⁴ Treadwell and Mayr, *Zeitsch. anorg. Chem.*, 1915, 92, 127.

⁵ See for example Dean, *J. Amer. Chem. Soc.*, 1918, 40, 619. For the estimation of sulphur in sodium sulphide, see Hassreidter, *Chem. Zeit.*, 1923, 47, 891; Berl and Pfannmüller, *ibid.*, 1924, 48, 115; in antimony sulphide, see Alcock, *Pharm. J.*, 1913, [iv.], 37, 213; Hutin, *Ann. Chim. anal.*, 1916, 21, 32; Luff and Porritt, *J. Soc. Chem. Ind.*, 1921, 40, 275; and in zinc blende, see Koelsch, *Chem. Zeit.*, 1916, 40, 174. For a summary of methods for the estimation of sulphur in iron pyrites, see Craig, *Chem. News*, 1917, 115, 253, 265; also Phillips, *ibid.*, 1917, 115, 312; Karaoglanow and Dimitrow, *Zeitsch. anal. Chem.*, 1917, 56, 561; Dittler, *Kolloid-Zeitsch.*, 1917, 21, 27; Zay, *Chem. Zentr.*, 1917, i., 446; Martin, *Mon. scient.*, 1918, [v.], 8, ii., 149; Bartsch, *Chem. Zeit.*, 1919, 43, 33; Chaudron and Juge-Boirard, *Compt. rend.*, 1922, 174, 683; Schon and Vykypiel, *Chem. Zeit.*, 1926, 50, 673; Hawes, *Min. and Met.*, 1927, 8, 462; Järvinen, *Zeitsch. anal. Chem.*, 1927, 72, 81; Kastner, *Ann. Chim. anal.*, 1927, [ii.], 9, 134. For sulphur in spent oxide, see Espenhahn, *J. Soc. Chem. Ind.*, 1916, 35, 292; Stavorinus, *Gas- u. Wasserfach*, 1926, 69, 790. For sulphur as sulphide in glass, see Heinrichs, *Zeitsch. anorg. Chem.*, 1927, 166, 299.

⁶ Willard and Fenwick, *J. Amer. Chem. Soc.*, 1923, 45, 645.

Insoluble sulphides must be examined by other processes of which examples are given under Sulphur (p. 48).

The Polysulphides.

Polysulphides of the Metals.—Sulphur shows a remarkable power of combining with metals, especially the alkali and alkaline earth metals, in proportions greater than the usually recognised equivalent; thus, the existence has been established of a complete series of polysulphides of general formula R_2S_x , where x ranges from 2 to 5 in the sodium series and from 2 to 6 in the potassium series.¹ Iron pyrites, FeS_2 , may be regarded as belonging to the class of polysulphides.

The simplest method, in practice, for the production of the alkali polysulphides is supplied by the interaction of sulphur and the alkali sulphide in hot aqueous or alcohol solution.² "Liver of sulphur," obtained by fusing sulphur with potassium carbonate,³ is, when freshly prepared, mainly a mixture of potassium polysulphides with potassium thiosulphate. Solutions of the hydroxides of the alkali or alkaline earth metals also dissolve sulphur, yielding solutions of the polysulphides and thiosulphates of the corresponding metals (see p. 37). When a suspension of sulphur in aqueous ammonia is treated with hydrogen sulphide in the absence of air, a red solution is obtained, which on cooling yields yellow crystals of *ammonium pentasulphide*, $(NH_4)_2S_5$.⁴ Bloxam claimed⁵ to have separated tetra-, penta-, hepta- and nona-sulphides in this way, whilst Thomas and Riding,⁶ using alcoholic ammonia, obtained only what they considered to be di-, penta- and hepta-sulphides. Mills and Robinson, however, were unable to obtain evidence of the formation of any polysulphide other than the penta-sulphide.

The solutions of these polysulphides are yellowish-brown, and on treatment with acid in the usual manner they yield hydrogen sulphide and a precipitate of sulphur. In many cases polysulphides of the alkali and alkaline earth metals have been isolated in the solid state; the types M_2S_4 and M_2S_5 appear to be the most stable as a general rule.⁷

Fused mixtures of alkali sulphide and sulphur attack glass, but not glazed porcelain, above $400^\circ C$.; ⁸ this action is greatest when the composition corresponds to the disulphide.

Alkali polysulphides react in solution with sodium sulphite, forming thiosulphate and sulphide; by determining the amount of thiosulphate

¹ Jones, *Trans. Chem. Soc.*, 1880, 37, 461; Hugot, *Compt. rend.*, 1899, 129, 388; Rosenfeld, *Ber.*, 1891, 24, 1660; Locke and Austell, *Amer. Chem. J.*, 1898, 20, 592; Thomas and Rule, *Trans. Chem. Soc.*, 1917, 111, 1063.

² Sabatier, *Ann. Chim. Phys.*, 1881, [v.], 22, 66; Böttger, *Annalen*, 1884, 223, 335; *Ber.*, 1884, 17, 308; Bloxam, *Proc. Chem. Soc.*, 1899, 15, 146; Spring and Demarteau, *Bull. Soc. chim.*, 1889, [iii.], 1, 312; Küster and Heberlein, *Zeitsch. anorg. Chem.*, 1905, 43, 53; Rule and Thomas, *Trans. Chem. Soc.*, 1914, 105, 2819.

³ See Liebig, *Annalen*, 1832, 2, 27; 1836, 18, 170.

⁴ Mills and Robinson, *J. Chem. Soc.*, 1928, p. 2326.

⁵ Bloxam, *Trans. Chem. Soc.*, 1895, 67, 277.

⁶ Thomas and Riding, *ibid.*, 1923, 123, 1726.

⁷ Rule and Thomas, *loc. cit.*; Barbieri, *Atti R. Accad. Lincei*, 1914, [v.], 23, ii., 8; Auld, *Trans. Chem. Soc.*, 1915, 107, 480; Guareschi, *Compt. rend.*, 1916, 163, 390; Biltz and Wilke-Dörfurt, *Zeitsch. anorg. Chem.*, 1906, 48, 297; Bloch and Höhn, *Ber.*, 1908, 41, 1961.

⁸ Thomas and Rule, *loc. cit.*

produced, the polysulphide sulphur in the original solution may be estimated.¹

Hydrogen Polysulphides.—In 1777 Scheele observed that by the rapid addition of much acid to a solution of sulphur in an alkali it was possible to produce a yellow, pungent, oily substance. Better conditions for the preparation of this substance were first described by Berzelius in 1825, who stated that a concentrated solution of "liver of sulphur" should be added in small quantities to dilute hydrochloric acid.² The oily substance, of specific gravity approx. 1.7, is very unstable and is rapidly decomposed on contact with water, although dilute acids, especially hydrochloric acid, exert a distinct preservative action. For many years the oil was regarded as hydrogen pentasulphide,³ H_2S_5 . When freshly prepared it is completely soluble in cold benzene; it cannot therefore contain any considerable quantity of free sulphur, and as its composition approximates to that of a pentasulphide, it was natural to come to the conclusion that it might be an impure hydrogen pentasulphide; now, however, the product is not regarded as a definite compound. It varies in viscosity according to the percentage of sulphur in the original dissolved metallic polysulphide, and widely divergent views have at various times been expressed as to the formula representing its composition.⁴

A discovery that certain alkaloids were capable of producing definite crystalline compounds with hydrogen polysulphide unfortunately failed to elucidate the mystery of the composition of the latter, since the compounds produced did not yield unanimous indications. Thus strychnine yielded a hexasulphide, $(C_{21}H_{22}O_2N_2)_2 \cdot H_2S_6$, whilst brucine gave two hexasulphides, a red one, $(C_{23}H_{23}O_4N_2)_3 \cdot (H_2S_6)_2$, and a yellow one, $(C_{23}H_{26}O_4N_2)_3 \cdot H_2S_6 \cdot 6H_2O$, and also an octasulphide, $C_{23}H_{26}O_4N_2 \cdot H_2S_8 \cdot 2H_2O$.⁵ Furthermore, apart from the fact that these additive compounds were not of one type and that their composition was at first wrongly interpreted, there was the additional disadvantage that their indications did not accord well with the earlier views concerning the formula of hydrogen polysulphide.

At the beginning of the twentieth century, therefore, there was no certainty as to the formula of hydrogen polysulphide, and, indeed, any formula between the limits H_2S_2 and H_2S_8 appeared possible, although the representation H_2S_5 appeared to be more in favour than any other. Three well-defined compounds, however, have now been isolated, *hydrogen disulphide*, H_2S_2 , *hydrogen trisulphide*, H_2S_3 , and *hydrogen pentasulphide*, H_2S_5 ; these will be described; there is also evidence of the existence of *hydrogen hexasulphide*, H_2S_6 . The alkaloid compounds already mentioned are well-crystallised, stable bodies, and furthermore, the solubility curves for sulphur in the disulphide and trisulphide respectively have been determined⁶ between the tempera-

¹ Wöber, *Zeitsch. angew. Chem.*, 1921, 34, 73; Kurtenacker and Bittner, *Zeitsch. anorg. Chem.*, 1925, 142, 115.

² See Thénard, *Ann. Chim. Phys.*, 1831, 47, 79; Liebig, *Annalen*, 1832, 2, 27; 1836, 18, 170.

³ Rebs, *Annalen*, 1888, 246, 356; *Ber.*, 1888, 21, 598.

⁴ Thénard, *loc. cit.*, (H_2S_5) ; Ramsay, *Trans. Chem. Soc.*, 1874, 12, 857, $(H_2S_7-H_2S_{10})$; Hofmann, *Ber.*, 1868, 1, 189, (H_2S_5) ; Sabatier, *Compt. rend.*, 1880, 91, 53, $(H_2S_6-H_2S_{10})$; 1885, 100, 1346, (H_2S_6) .

⁵ Hofmann, *Ber.*, 1868, 1, 189; 1877, 10, 1067; Schmidt, *Bull. Soc. chim.*, 1876, 26, 218; *Annalen*, 1876, 180, 287; *Ber.*, 1877, 10, 1289.

⁶ Walton and Whitford, *J. Amer. Chem. Soc.*, 1923, 45, 601.

tures -84.72°C. and 55.8°C. and found to be identical; in both cases there is a marked break in the curve at -1.45°C. , at which temperature the liquid has a composition very near to that required by the formula H_2S_8 (i.e. 82.47 per cent. of sulphur not evolved as H_2S); (see fig. 6).

Preparation.—The crude hydrogen polysulphide, or "hydrogen persulphide" as it is frequently termed, is best prepared by heating for three hours at 100°C. a mixture of sodium sulphide, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, with half its weight of sulphur. The crystalline sulphide melts and the sulphur is gradually dissolved to a deep-red solution of which the solute has a composition between Na_2S_4 and Na_2S_5 . This solution is mixed with rather less than its own bulk of water and is then introduced as a thin stream into a mixture of dilute hydrochloric acid and ice. The same yellow, oily product is obtained whatever the composition of the dissolved polysulphide, whether Na_2S_2 , Na_2S_3 , Na_2S_4 or Na_2S_5 .¹

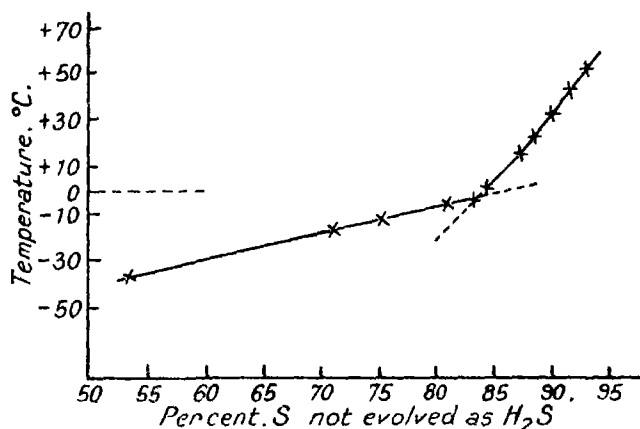


FIG. 6.—Solubility of Sulphur in Hydrogen Di- and Tri-sulphides

If the oil is distilled under a pressure of 2 mm. in glass apparatus of which the superficial alkali has been removed by treatment with hydrogen chloride (see p. 70), a distillate amounting to approximately one-sixth of the original bulk can be collected in the usual manner and on analysis proves to be *hydrogen trisulphide*, H_2S_3 . At the same time a more volatile liquid, actually *hydrogen disulphide*, H_2S_2 , can be condensed in a second receiver cooled by a mixture of ether and solid carbon dioxide.²

The crude persulphide is also formed together with a large proportion of sulphur, when sulphur dioxide either as gas or in solution is reduced by means of hypophosphorous acid.³

The *pentasulphide*, H_2S_5 , has been isolated more recently⁴ by decomposing pure anhydrous ammonium pentasulphide with anhydrous formic acid (see p. 70).

General Properties.—All the known hydrogen polysulphides, as well

¹ Bruni and Borgo, *Atti R. Accad. Lincei*, 1907, [v.], 16, ii., 745; Paternò, *ibid.*, 1908, [v.], 17, ii., 627; Walton and Parsons, *J. Amer. Chem. Soc.*, 1921, 43, 2539.

² Bloch and Hohn, *Ber.*, 1908, 41, 1961, 1971, 1975, 1980.

³ von Dienes, *Annalen*, 1924, 440, 213.

⁴ Mills and Robinson, *J. Chem. Soc.*, 1928, p. 2326.

as the crude so-called hydrogen persulphide, are yellow liquids at the ordinary temperature. They are very sensitive towards alkalis, and it is therefore necessary to treat glass vessels intended for their storage (which is often possible only for a few hours) with hydrogen chloride gas. If necessary, the compounds can be dried over calcium chloride, but this also should have received previous treatment with hydrogen chloride.¹

The compounds burn with a blue flame, giving water and sulphur dioxide. Even at the ordinary temperature they readily decompose into hydrogen sulphide and sulphur,² the measurement of the amount of hydrogen sulphide formed from a known weight of a hydrogen polysulphide, when warmed in an atmosphere of hydrogen, supplying the most convenient method of analysis. Dilute acids act as preservatives, but even traces of alkali cause rapid and vigorous decomposition. The addition of alcohols, especially amyl alcohol, also induces rapid decomposition.

Sulphur dissolves in the various hydrogen polysulphides as already described;³ the solutions deposit crystalline sulphur when cooled or on the addition of benzene.⁴ As solutions of sulphur in hydrogen disulphide or trisulphide behave in this way, whereas the fresh crude polysulphide does not yield its excess of sulphur on similar treatment, this supplies further evidence of the existence of a higher polysulphide in the crude "persulphide."

The hydrogen polysulphides are miscible with benzene, toluene, chloroform, bromoform, carbon disulphide, ether and heptane, giving relatively stable solutions,⁵ and the use of such solutions has been suggested in place of sulphur chloride for the vulcanisation of caoutchouc at the ordinary temperature. The addition of alcohol to the benzene solutions induces rapid decomposition, with formation of nacreous sulphur, which slowly undergoes conversion into ordinary sulphur (p. 25). Ketones, nitrobenzene, aniline and pyridine also catalyse the decomposition.

Hydrogen Pentasulphide, H_2S_5 ,⁶ is a thin, pale yellow oil, obtained by treating pure dry ammonium pentasulphide crystals with carefully dried formic acid. No free sulphur is produced in this preparation as is the case when a mineral acid, or even 90 per cent. formic acid, is used. The liquid has a density of 1.67 at 16° C. Cryoscopic measurements in benzene give the molecular weight as 152.5; H_2S_5 requires 162. It cannot be distilled, but at 40° C. and 15 mm. it froths considerably. On cooling it suddenly becomes viscous at -25° C., almost solid at -85° C. and glassy at -50° C., melting to a clear liquid again on warming. It readily dissolves sulphur.

Hydrogen Trisulphide, H_2S_3 , distils from the crude "persulphide" at approximately 69° C. when the pressure is reduced to 2 mm. It is a pale yellow mobile oil at the ordinary temperature, but on cooling becomes colourless, whilst when warmed it becomes more viscous and

¹ Bloch and Höhn, *loc. cit.*

² Kemp, *Phil. Mag.*, 1838, 7, 144; *Annalen*, 1838, 28, 170.

³ Walton and Whitford, *loc. cit.*; Walton and Parsons, *loc. cit.*

⁴ Bruni and Borgo, *Atti R. Accad. Lincei*, 1908, [v.], 18, 1., 356.

⁵ Drechsel, *J. prakt. Chem.*, 1871, [ii.], 4, 20; Bloch and Höhn, *loc. cit.*; Walton and Parsons, *loc. cit.*

⁶ Mills and Robinson, *J. Chem. Soc.*, 1928, p. 2326.

deepens in colour; at 90° C. decomposition sets in, accompanied by a vigorous evolution of hydrogen sulphide.¹ Under atmospheric pressure at ordinary temperatures it undergoes slow decomposition, the escape of hydrogen sulphide causing it to foam. The liquid has a disagreeable pungent odour, suggesting camphor and sulphur chloride; its vapour has an irritating effect on the eyes and nose. The density is 1.496. On strong cooling (−75° C.) the liquid yields a crystalline mass after passing through a very viscous stage, no sharp solidifying-point being apparent; on warming again, however, there is a short delay at −53° to −52° C. in the rise of temperature.² In bromoform solution the molecular weight by cryoscopic measurement has been found to agree with the formula H_2S_3 .³ The oil is soluble in liquid hydrogen sulphide.

Hydrogen trisulphide is much more easily combustible than the crude parent hydrogen polysulphide. Exposure to light tends to accelerate its decomposition. It slowly reduces concentrated sulphuric acid to sulphur dioxide, whilst on contact with dry silver oxide, cupric oxide, lead dioxide or mercuric oxide, it bursts into explosive combustion,² a residue of the metallic sulphide being obtained. Many other metallic oxides and most salts bring about a less vigorous decomposition; metals in the massive condition only react with it slowly. With potassium permanganate or dichromate the reaction is violent.

Hydrogen Disulphide, H_2S_2 , in addition to being obtained from the distillation of crude "hydrogen persulphide," is also formed when hydrogen trisulphide is distilled at 100° C. under a pressure of 20 mm.; approximately one-third of the trisulphide is converted into disulphide, whilst the remainder passes into hydrogen sulphide and sulphur. The disulphide, therefore, is the most stable of the hydrogen polysulphides towards heat, and can actually be distilled under atmospheric pressure at 71° to 75° C. with only partial decomposition.

It is a clear yellow liquid, of density 1.327 at 25° C.; its vapour is much more pungent than that of the trisulphide and more severely attacks the eyes and mucous membranes. The melting-point is −89.6° C.,⁴ and the boiling-point 70.7° C.⁴ It is soluble in the same solvents as the trisulphide.

Towards alkalis the disulphide is much less stable than the trisulphide and decomposes almost explosively in an untreated glass flask. Distilled water induces rapid decomposition, whilst contact with alkali causes explosive formation of hydrogen sulphide. When placed on paper or on the skin, rapid decomposition occurs, in the latter case with formation of a white fleck, resembling the effect of hydrogen peroxide. The disulphide resembles the trisulphide in its behaviour with sulphuric acid and with silver oxide; it is more readily inflamed than the trisulphide.

Constitution.—From the composition of hydrogen disulphide and its chemical behaviour, it is natural to regard it as the analogue of hydrogen peroxide, and as having therefore the structure $H \cdot S \cdot S \cdot H$.⁵ It is probable that the higher polysulphides are of a similar "chain"

¹ Bloch and Hohn, *loc. cit.*, p. 1971.

² Walton and Parsons, *loc. cit.*

³ Schenck and Falcke, *Ber.*, 1908, 41, 2600.

⁴ Butler and Maass, *J. Amer. Chem. Soc.*, 1930, 52, 2184; Walton and Parsons, *loc. cit.*

⁵ See Dodonov and Medox, *Ber.*, 1928, 61, [B], 1767.

type,¹ that is, of constitutions $\text{H}\cdot\text{S}\cdot\text{S}\cdot\text{S}\cdot\text{H}$, $\text{H}\cdot\text{S}\cdot\text{S}\cdot\text{S}\cdot\text{S}\cdot\text{H}$, and the missing member of this series, H_2S_4 , may be present, in addition to hydrogen pentasulphide, in crude hydrogen persulphide.

On the other hand, the suggestion has been made that the polysulphides are analogous in structure to the periodides and are to be represented as additive compounds of hydrogen sulphide with sulphur of the general formula $\text{H}_2\text{S} \cdot \text{S}_n$.² In such a case, the additional sulphur atoms

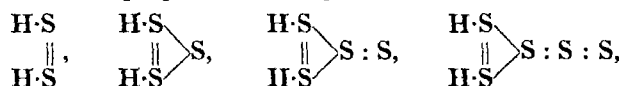
would presumably be attached in the manner $\begin{array}{c} \text{H} \\ \diagup \\ \text{S} : \text{S} \\ \diagdown \\ \text{H} \end{array}$, $\begin{array}{c} \text{H} \\ \diagup \\ \text{S} : \text{S} : \text{S} \\ \diagdown \\ \text{H} \end{array}$,

etc. This view possesses an advantage in giving a possible reason why hydrogen disulphide should be more stable than the higher polysulphides towards rise in temperature, because, of the polysulphides, it alone would be free from a quadrivalent sulphur atom with its four valencies entirely satisfied by other sulphur atoms. Indeed, the change in colour of hydrogen trisulphide with alteration of temperature, as well as the low stability of the trisulphide relative to the disulphide at higher temperatures, have been tentatively referred to the existence of dynamic

isomerism³ between the two structures $\text{H}\cdot\text{S}\cdot\text{S}\cdot\text{S}\cdot\text{H} \rightleftharpoons \begin{array}{c} \text{H} \\ \diagup \\ \text{S} : \text{S} : \text{S} \\ \diagdown \\ \text{H} \end{array}$.

The evidence, however, is very slight, and this suggestion, together with that of a structure $\begin{array}{c} \text{S} & \text{SH} \\ & \diagdown \quad \diagup \\ & \text{S} \\ & \diagup \quad \diagdown \\ \text{S} & \text{SH} \end{array}$ for hydrogen pentasulphide, making the latter structurally analogous to sulphuric acid,⁴ must be regarded as requiring experimental confirmation before serious consideration can be claimed.

An alternative method of representing the formulae of the polysulphides has been proposed,⁵ namely



and this shares with the earlier $\text{H}_2\text{S} \cdot \text{S}_n$ formula the advantage of indicating a possible reason for the relatively greater stability of hydrogen disulphide at higher temperatures. This type of constitution is favoured also by the behaviour of the polysulphides of sodium and potassium when heated in hydrogen. Sulphur is readily removed from the higher sulphides, but the disulphides of both metals are very stable compounds from which sulphur can only be removed with difficulty at 700° to 800°C .⁶

The evidence supplied by the organic polysulphides⁷ corresponding with hydrogen disulphide, trisulphide, etc., appears, however, to be strongly in favour of the "chain" structure mentioned at the commencement of this discussion. Hydrogen disulphide and trisulphide form additive compounds with aromatic aldehydes such as benzaldehyde,

¹ Küster and Heberlein, *Zeitsch. anorg. Chem.*, 1905, 43, 53.

² Küster, *ibid.*, 1905, 44, 431; 46, 113. ³ Bloch and Höhn, *loc. cit.*, p. 1980.

⁴ Erdmann, *Annalen*, 1908, 362, 133; Drechsel, *J. prakt. Chem.*, 1871, [ii.], 4, 20; Jones, *Trans. Chem. Soc.*, 1880, 37, 461.

⁵ Auld, *Trans. Chem. Soc.*, 1915, 107, 480. See also Bodnár, *Chem. Zeit.*, 1915, 39, 715.

⁶ Thomas and Rule, *Trans. Chem. Soc.*, 1917, 111, 1063.

⁷ Blanksma, *Rec. Trav. chim.*, 1901, 20, 121, 141; Holmberg, *Annalen*, 1907, 359, 81; Strecker, *Ber.*, 1908, 41, 1105; Smythe, *Trans. Chem. Soc.*, 1914, 105, 546.

e.g. $(C_6H_5CHO)_2.H_2S_2$, $(C_6H_5CHO)_2.H_2S_3$, and the behaviour of these products indicates that the sulphur atoms are present in a continuous chain.¹ In the light of our present knowledge, therefore, the most satisfactory method of representing the constitution of the hydrogen polysulphides is by means of the "sulphur chain" formulæ.

HALIDES AND OXYHALIDES OF SULPHUR.

As towards hydrogen so towards sulphur the affinity of the halogen elements rapidly decreases on passing from fluorine to iodine. Sulphur hexafluoride, SF_6 , is a stable substance, whereas the highest chlorine derivative which has been isolated is the unstable tetrachloride, SCl_4 ; sulphur monobromide, S_2Br_2 , is the only bromide of sulphur known, whilst sulphur and iodine do not form any definite compound.

Sulphur Monofluoride or Disulphur Difluoride, S_2F_2 .—When dry silver or mercurous fluoride and sulphur are heated together in a vacuum, a gas is evolved which is believed to be sulphur monofluoride, S_2F_2 .² The fluoride is a colourless gas with an odour similar to that of sulphur monochloride; it is decomposed by moisture with deposition of sulphur. On keeping, the gas yields a yellow or white deposit, the separation of which is complete after 12 to 14 hours, the gas afterwards appearing to be stable at ordinary temperatures. That sulphur monofluoride is not completely stable towards heat is indicated by molecular weight determinations. Samples prepared from silver fluoride gave the results 93.0, 93.2, 94.6, whilst a sample prepared at a higher temperature from mercurous fluoride gave a molecular weight of 86.

At low temperatures the gas yields a snow-like solid which melts at $-105.5^\circ C$. The density of the liquid at $-100^\circ C$. is 1.5. The approximate boiling-point is $-99^\circ C$.

Sulphur monofluoride may be used in a similar manner to the monochloride for the vulcanisation of caoutchouc.

Sulphur Tetrafluoride, SF_4 , has been prepared³ by heating at $120^\circ C$. a mixture of cobalt trifluoride, fluorspar and sulphur. It is a colourless gas, which may be condensed to a liquid in a vessel surrounded by liquid air.

Sulphur Hexafluoride, SF_6 .—Sulphur hexafluoride, the first hexahalide to be discovered, is prepared by submitting sulphur to the action of fluorine in a copper tube. The issuing gas on condensation in a spiral tube of the same metal at $-80^\circ C$. becomes partly solidified; by allowing the solid to vaporise gradually and passing the vapours through potassium hydroxide solution and solid potassium hydroxide successively, the substance is rendered purer, complete purification being effected subsequently by re-solidification followed by fractional evaporation.⁴

Sulphur hexafluoride is a colourless, odourless and incombustible gas of density 5.08 (air = 1). When solidified it forms a colourless crystalline mass of melting-point $-56^\circ C$. As the vapour pressure of the solid attains one atmosphere at $-62^\circ C$. the solid has no melting-point

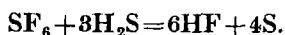
¹ Brunner and Vuilleumier, *Schweiz. Woch. Chem. Pharm.*, 1908, 46, 436; *Abstr. Chem. Soc.*, 1908, 94, i., 900; Bloch, Höhn and Bugge, *J. prakt. Chem.*, 1910, [ii.], 82, 473; Bugge and Bloch, *ibid.*, 1910, [ii.], 82, 512.

² Centnerszwer and Strenk, *Ber.*, 1923, 56, [B], 2249; 1925, 58, 914.

³ Fischer, *Zeitsch. angew. Chem.*, 1929, 42, 810.

⁴ Moissan and Lebeau, *Compt. rend.*, 1900, 130, 865.

under ordinary pressures but volatilises without melting. The critical temperature is $+54^{\circ}\text{C}$.¹ The gas is only sparingly soluble in alcohol or water. It is remarkably inert, approaching even nitrogen in this respect.² It is unaffected by the silent electric discharge, and even the spark discharge causes only slight decomposition. Mixed with hydrogen it withstands a high temperature, but under the influence of powerful electric sparks formation of hydrogen sulphide and hydrogen fluoride can be effected. At a red heat copper and silver are without action on the gas, although magnesium and sodium effect its decomposition; at lower temperatures, however, it resists even these two metals and sodium can be melted unchanged in an atmosphere of the gas, as also can the hydroxides of the alkali metals. Hydrogen chloride and ammonia are unaffected by sulphur hexafluoride, but hydrogen sulphide reacts rapidly according to the equation:



The Chlorides of Sulphur.

That chlorine can unite with sulphur was observed by Hagemann in 1782, and that the chlorination of sulphur may take place in at least two stages was known to Berthollet in 1807, the orange substance first produced yielding, on further chlorination, a red product. This was confirmed by Dumas in 1832, who showed that the compositions and vapour densities of the liquids saturated with sulphur and chlorine, respectively agreed with the formulae S_2Cl_2 and SCl_2 , using modern values for atomic weights. The variable composition of the red chloride, however, has led chemists to the conclusion that it is not a chemical entity, but a mixture of S_2Cl_2 and SCl_2 , the substance SCl_2 apparently being unable to exist under ordinary conditions.

A careful study of the equilibria involved³ at the freezing-points of the chlorides of sulphur has recently shown that four distinct chlorides are capable of existence, namely S_2Cl_2 , S_3Cl_4 , SCl_2 and SCl_4 . The freezing-point curves are shown in fig. 7. The fact that several different compounds could separate from the mixtures within the range S_2Cl_2 to SCl_4 was clearly indicated by the appearance of the solid phase.

Sulphur monochloride separated in granular form from mixtures containing fewer than 56.6 atoms of chlorine per cent. (i.e. 59.1 per cent. chlorine).

Trisulphur tetrachloride separated over the narrow range of 56.6 to 59.2 atoms of chlorine per cent. (i.e. 61.6 per cent. chlorine) after seeding with a sample cooled in liquid air to prevent the separation of a liquid phase. It was of a flocculent nature, very different from the granular monochloride or the pasty dichloride. As this different appearance coincided with the limits of a section of the broken freezing-point curve, it was regarded as evidence of the separation of a compound intermediate in composition between the monochloride and dichloride.

Sulphur dichloride separated as a finely divided buff-yellow powder from mixtures containing 59.2 to 64.9 atoms of chlorine per cent. (i.e. 61.6 to 67.2 per cent. chlorine). A portion was recrystallised from light petroleum at low temperatures and its composition confirmed by analysis.

¹ Prideaux, *Trans. Chem. Soc.*, 1906, 89, 316; Moissan and Lebeau, *loc. cit.*

² Compare Berthelot, *Ann. Chim. Phys.*, 1900, [vii.], 21, 205.

³ Lowry, McHatten and Jones, *J. Chem. Soc.*, 1927, p. 746.

Sulphur tetrachloride separated in butter-like form from mixtures containing more than 64.9 atoms of chlorine per cent. (i.e. 67.2 per cent. chlorine).

A study of the subject is rendered difficult by the fact that several equilibria are involved. These equilibria appear in some cases to be slow of attainment, a fact that serves to explain contradictory results by different investigators.

It has been concluded¹ that the equilibrium of the chlorides of sulphur in the middle regions of concentration is dominated by two

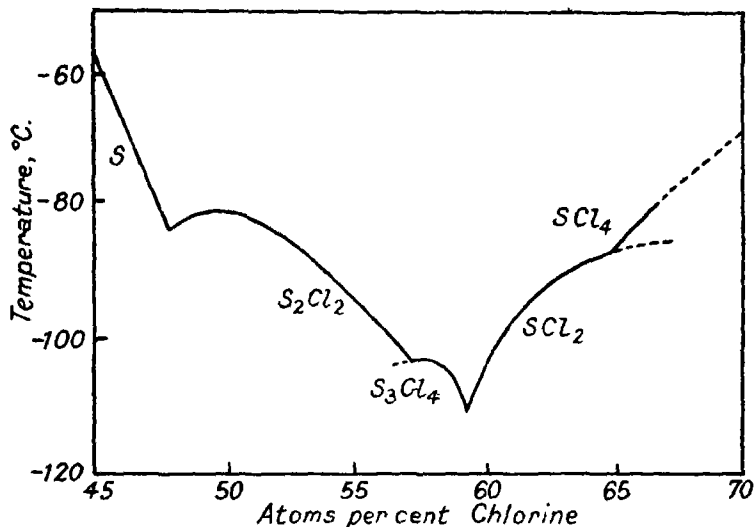
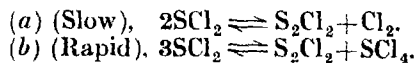


FIG. 7.—Freezing-points of the Chlorides of Sulphur.

simultaneous dissociations of the dichloride, proceeding at very unequal rates, namely :



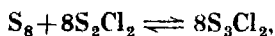
This would serve to explain the otherwise puzzling observation that, although an equilibrium mixture having the composition of sulphur dichloride deposits sulphur tetrachloride on freezing, freshly prepared mixtures of sulphur monochloride with an over-chlorinated sample of sulphur dichloride exhibit a maximum freezing-point at the composition SCl_2 , which disappears when the mixture is brought to a condition of equilibrium. The rapid initial production of sulphur dichloride, in accordance with the foregoing equation (b), is presumably followed by the slower process of destruction indicated by equation (a). When chlorine is passed into sulphur monochloride at ordinary temperatures, absorption ceases when the liquid contains about 70 per cent. of chlorine ($\text{SCl}_2 = 68.9$ per cent. chlorine), but at 0°C . absorption continues beyond this point.² The reaction proceeds more rapidly in direct sunlight, and is catalysed by antimony pentachloride.

In addition to the foregoing, evidence has been obtained of the

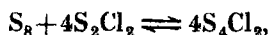
¹ Lowry and coworkers, *loc. cit.*

² Bothamley, *Trans. Faraday Soc.*, 1928, 24, 47.

existence of *sulphur subchlorides*, probably S_4Cl_2 and S_3Cl_2 . When a mixture of sulphur and sulphur monochloride is dissolved in bromoform, the lowering of the freezing-point is less than the sum of the depressions produced by the two solutes separately.¹ This is apparently due to the presence of sulphur subchlorides in equilibrium with their components. Moreover, the composition of a saturated solution of sulphur in sulphur monochloride corresponds approximately with the formula S_4Cl_2 , and a study of the boiling-points of solutions containing increasing concentrations of sulphur in the monochloride suggests that such reactions as the following may occur :²



and

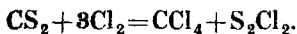


the latter reaction predominating when the sulphur concentration is high. The solubility of the sulphur at any given temperature is increased by previously heating the solution to a higher temperature, the increase being greater the higher the temperature of preheating.³

Sulphur Monochloride or Disulphur Dichloride, S_2Cl_2 , the initial product of the combination of sulphur and chlorine, was first thoroughly studied in 1810 by Davy and Buchholz, independently.

Preparation.—Sulphur and chlorine interact slowly at the ordinary temperature but much more readily on warming. The customary procedure is to pass dried chlorine into fused sulphur or over dry "flowers of sulphur" until most of the sulphur has disappeared. The resulting monochloride contains considerable amounts of higher sulphur chlorides in solution, but if the mixture is heated for some time under a reflux condenser the pure monochloride can subsequently be distilled over.

Industrially, much sulphur monochloride is obtained as a by-product in the manufacture of carbon tetrachloride by the action of chlorine on carbon disulphide in the presence of a suitable catalyst, e.g. iodine :⁴



Various other processes can be made to yield sulphur monochloride. The distillation of sulphur with stannous chloride or mercuric chloride yields sulphur monochloride and, indeed, may be regarded as a modification of the method first given. The action of phosphorus pentachloride on sulphur or on metallic sulphides and the action of chlorine on metallic sulphides form closely analogous processes, especially in view of the formation of chlorine as a dissociation product from phosphorus pentachloride. With phosphorus pentachloride the phosphorus is found finally as sulphochloride. Of other methods there may be mentioned the interaction of sulphur or of phosphorus sulphide with thionyl chloride,⁵ and the action of dry chlorine on a hot or boiling solution of

¹ Bruni and Amadori, *Atti R. Accad. Lincei*, 1919, [v.], 28, i., 217.

² Ruff and Golla, *Zeitsch. anorg. Chem.*, 1924, 138, 33. See also Bruni, *ibid.*, 1925, 149, 387; Trautz and others, *Zeitsch. Elektrochem.*, 1929, 35, 110.

³ Hammick and Zvegintsov, *J. Chem. Soc.*, 1928, p. 1785; Aten, *Zeitsch. physikal. Chem.*, 1913, 81, 257.

⁴ Weber, *Ann. Phys. Chem.*, 1866, [ii.], 128, 559.

⁵ Carius, *Annalen*, 1858, 106, 331.

sulphur in sulphur dichloride ¹ or on a strongly heated mixture of barium sulphate with coal, coke or hydrocarbons of high carbon content.²

The monochloride may be obtained in a highly purified condition by mixing a high-grade commercial sample with 1 per cent. by weight of a mixture of highly absorbent charcoal and sulphur, distilling in glass apparatus and collecting the fraction distilling above 137° C. This fraction, after addition of more charcoal and sulphur, is redistilled in a vacuum under a pressure of 28 mm., pure sulphur monochloride distilling at 41° C.³

Physical Properties.—Sulphur monochloride is a golden-yellow liquid which fumes in moist air; it has an unpleasant pungent odour and a hot, bitter taste. At 25° C. the density of the liquid is 1.67328; ⁴ the surface tension, measured at 22° C. by the capillary rise method, is 40.78; the relative viscosity at 18° C. is 1.908, and the specific heat at 22° C. is 0.22 (± 2.8 per cent.).⁵ The boiling-point is 138° C. and the melting-point -76° to -75° C.⁶ The vapour pressure through the temperature range 0° to 138° C. is given in the following table: ⁷

° C.	Vapour Pressure in mm. (P.).	° C.	Vapour Pressure in mm. (P.).	° C.	Vapour Pressure in mm. (P.).
0	3.7	50	43.0	100	257.0
10	6.4	59	60.0	110	351.5
20	10.7	70	93.0	120	469.7
31	18.6	80	135.0	130	615.2
40	28.0	90	186.4	138	760.0

The equation for the corresponding curve is :

$$\log_{10} P = 7.4550 - 1880.1/T \quad (T = \text{abs. temp.}),$$

from which the latent heat of evaporation is calculated to be 63.9 cal./gm. or 8626.5 cal./mol., and the molecular boiling-point elevation constant is 52.9.⁸ Under the foregoing conditions sulphur monochloride is a stable, well-defined compound.

The monochloride exhibits a slight tendency to molecular dissociation,⁹ but the effect is so small that both in the dissolved and in the gaseous condition the molecular weight agrees with the formula S_2Cl_2 . As it does not combine with bromine, ebullioscopic determinations of

¹ Terlinck, *French Patent*, 611141 (1925); *Chem. Zeit.*, 1927, 51, 861.

² *Chem. Fabr. Griesheim-Elektron*, Assecs. of K. L. Gonder, *German Patent*, 417853 (1922).

³ Harvey and Schuette, *J. Amer. Chem. Soc.*, 1926, 48, 2065.

⁴ Harvey and Schuette, *loc. cit.*; Fawsitt (*J. Soc. Chem. Ind.*, 1886, 5, 638) gives the density at 0° C. as 1.706, and at 15° C. as 1.683; Kretov (*J. Chem. Ind. Moscow*, 1928, 5, 1268) gives $d_{20}^{20} = 1.6824$.

⁵ Trautz and others, *Zeitsch. Elektrochem.*, 1929, 35, 110.

⁶ Beckmann, *Zeitsch. physikal. Chem.*, 1909, 65, 289; Frank and Marckwald, *Gummi. Zeit.*, 1914, 28, 1580; Roozeboom, *Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 63; Aten, *Zeitsch. physikal. Chem.*, 1905, 54, 55.

⁷ Harvey and Schuette, *loc. cit.*; cf. Trautz and others, *loc. cit.*

⁸ Cf. Orndorff and Terrasse, *Amer. Chem. J.*, 1896, 18, 173; Beckmann, *loc. cit.*

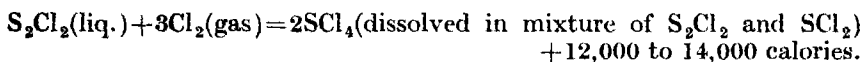
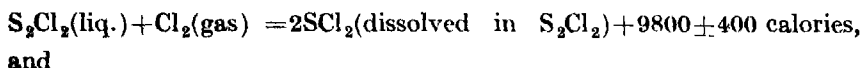
⁹ Beason and Fournier, *Compt. rend.*, 1910, 150, 1752.

the molecular weight have been made in this solvent, and also even in liquid chlorine (see p. 81).

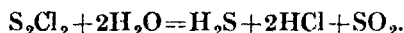
The compound is exothermic : ¹



Sulphur monochloride is soluble in many organic solvents, *e.g.* carbon disulphide, benzene, carbon tetrachloride and light petroleum ; it also possesses solvent properties, dissolving sulphur, very readily on warming and slowly depositing much of the solid on cooling ; the molecular heat of solution of sulphur in sulphur monochloride is from -1300 to -3000 calories (see p. 76).² Chlorine, bromine and iodine are also dissolved, the two latter without chemical change ; with chlorine, however, combination occurs readily at the ordinary temperature, although at the boiling-point of liquid chlorine simple solution occurs primarily (see before and p. 81). The heat of solution of chlorine in sulphur monochloride is shown in the following equations : ³



Chemical Properties.—Sulphur monochloride will not burn under ordinary conditions in the air, but when passed through a red-hot tube in the vapour condition and mixed with air or oxygen, combustion occurs, accompanied by a greenish-blue flame and the formation of sulphur dioxide and trioxide, together with chlorine. In contact with water the monochloride undergoes decomposition according to the equation : ⁴



Even in the presence of a large excess of water decomposition only proceeds to the extent of 93.68 per cent., being partly restrained by the presence of the hydrogen chloride formed. The other factor which influences the extent of the action is the sulphur formed by subsequent reaction between the hydrogen sulphide and the sulphur dioxide. Polythionic acids are formed in solution and the sulphur which separates encloses undecomposed chloride and may also dissolve in it.⁵

With phosphorus the reaction products vary according to the conditions. In the presence of an excess of monochloride, phosphorus sulphochloride and free sulphur are obtained, whereas if the monochloride is introduced into an excess of molten phosphorus, the products are the trichloride and sulphide of phosphorus, some red phosphorus also being formed.⁶

¹ Thomsen, *Thermochemische Untersuchungen*, 1906, p. 188 ; Ogier, *Compt. rend.*, 1881, 92, 922. Trautz and his coworkers (*loc. cit.*) give 14.5 ± 0.4 Cals.

² See also Beckmann, *Zeitsch. physikal. Chem.*, 1909, 65, 289.

³ Trautz and others, *loc. cit.*

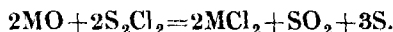
⁴ Carius, *Annalen*, 1858, 106, 291 ; Olin, *J. Amer. Chem. Soc.*, 1926, 48, 167.

⁵ Neumann and Fuohs, *Zeitsch. angew. Chem.*, 1925, 38, 277 ; Noack, *Zeitsch. anorg. Chem.*, 1925, 146, 239.

⁶ de Claubry, *Ann. Chim. Phys.*, 1843, [iii.], 7, 213 ; Wohler, *Annalen*, 1855, 93, 274 ; *Ann. Chim. Phys.*, 1855, [iii.], 44, 56 ; Chevreton, *Compt. rend.*, 1867, 64, 302 ; Michaelis, *Bull. Soc. chim.*, 1871, 15, 185.

With regard to the general reaction of sulphur monochloride with metals, Domanicki¹ has stated that univalent metals do not react, and bivalent metals, with the exception of mercury, if they react at all, do so with much greater difficulty than ter- or quadri-valent metals. There are other important exceptions to this rule, however; silver is slightly attacked by the monochloride, whilst copper and manganese are very considerably attacked. On the other hand, cobalt and chromium are unaffected, and it has been suggested that drums made of alloy or plated steel provide suitable containers for sulphur monochloride.² The corrosive action is greatly accelerated by the presence of dry ether, with which the metallic chlorides form complexes, thus enhancing the thermal effect of the action.

Many metallic oxides, especially those yielding volatile chlorides, are attacked by the vapour of sulphur monochloride, and the reaction forms a useful method for the conversion of such oxides into the corresponding anhydrous chlorides.³ Assuming a bivalent metal M, the change is:



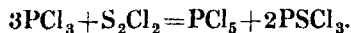
Such treatment can be extended to mineral substances, some of which at 800° C. under the action of sulphur monochloride vapour are easily convertible into the corresponding metallic chlorides.⁴

Sulphur trioxide and sulphur monochloride react to give pyrosulphuryl chloride, $S_2O_5Cl_2$, whilst sulphates when heated in the monochloride vapour are converted into chlorides⁵ in the following manner:



Under the influence of the silent discharge sulphur monochloride vapour is reduced by hydrogen to hydrogen chloride and sulphur or hydrogen sulphide.⁶ Hydriodic acid effects a similar reduction⁷ at the ordinary temperature, the products being hydrochloric acid, sulphur and hydrogen sulphide, together with iodine.

Phosphorus trichloride reacts with sulphur monochloride, iodine acting as a catalyst; the products are phosphorus pentachloride and phosphorus sulphochloride:⁸



Antimony pentachloride reacts to form the compound $SbCl_5 \cdot SCl_4$, which may be obtained as amber-coloured crystals.⁹

When an ice-cold solution of ammonia in chloroform is added to

¹ Domanicki, *J. Russ. Phys. Chem. Soc.*, 1916, 48, 1724.

² Harvey, *Chem. Met. Eng.*, 1928, 35, 684.

³ Bournon, *Ann. Chim. Phys.*, 1910, [viii.], 21, 56; *Compt. rend.*, 1907, 145, 62; 1909, 148, 170; Hicks, *J. Amer. Chem. Soc.*, 1911, 35, 1492.

⁴ E. F. Smith, *J. Amer. Chem. Soc.*, 1898, 20, 289; Hall, *ibid.*, 1904, 26, 1243; Hicks, *ibid.*, 1911, 33, 1492; Lukens, *ibid.*, 1913, 35, 1464; Serra, *Gazzetta*, 1899, 29, 355; Oddo and Giachery, *ibid.*, 1923, 53, 1, 63; Bournon, *Ann. Chim. Phys.*, 1910, 20, 547; Budnikov and Schilov, *Chem. Zentr.*, 1925, ii., 388.

⁵ Carius, *Annalen*, 1858, 106, 291.

⁶ Besson and Fournier, *loc. cit.*

⁷ Hautefeuille, *Bull. Soc. chim.*, 1867, [ii.], 7, 198.

⁸ Michaelis, *ibid.*, 1871, 15, 185; Kohn and Ostersetzter, *Zeitsch. anorg. Chem.*, 1913, 82, 240.

⁹ Partington, *J. Chem. Soc.*, 1920, p. 2573.

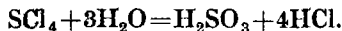
of this process is to saturate the monochloride, cooled in a freezing mixture, with chlorine and subsequently remove excess of the latter gas by a stream of carbon dioxide. Powdered absorbent charcoal acts catalytically in facilitating the action.¹ As prepared in this way, the mixture is a deep, reddish-brown liquid, of density 1.622 at 15° C.² It boils at 59° C. under atmospheric pressure, and at -24° C. under 4 mm., but on account of the very considerable dissociation into monochloride and chlorine, the boiling-point is not constant. When cooled, it solidifies near -88° C. and remelts at -78° C.³

Sulphur dichloride is decomposed by water, giving hydrochloric and thiosulphuric acids, the latter gradually yielding sulphurous acid and sulphur. This recalls the corresponding behaviour of the monochloride, and, probably on account of the considerable dissociation, even in the liquid condition, the chemical properties of the "dichloride" are generally similar to those of the monochloride.

Sulphur Tetrachloride, SCl_4 .—When a mixture of sulphur monochloride with liquid chlorine is kept in a sealed tube, slow combination ensues, with formation of sulphur tetrachloride. At ordinary temperatures the rate of combination is very slow, but it is hastened by a moderate rise in temperature.⁴

The product is a brownish-red liquid at ordinary temperatures; when cooled it exhibits in a marked manner the phenomenon of "suspended transformation," and generally does not solidify above -70° C., the yellowish-white solid obtained below this temperature melting at -30.5° C. A few degrees above the melting-point the dissociation pressure reaches one atmosphere, so that dissociation into sulphur monochloride and chlorine, probably with the production of sulphur dichloride as an intermediate stage, occurs exceedingly readily, and at the ordinary temperature the liquid contains only a small proportion of the tetrachloride, the dissociation products⁵ preponderating (see the following).

Water causes immediate and almost quantitative decomposition of sulphur tetrachloride, with formation of hydrochloric and sulphurous acids, the latter standing in the same relation to sulphur tetrachloride as carbonic acid to carbon tetrachloride and silicic acid to silicon tetrachloride:



With anhydrous ammonia the tetrachloride reacts to form nitrogen sulphide:⁶



With an equimolecular proportion of sulphur trioxide, interaction occurs forming thionyl chloride, sulphur dioxide and chlorine:



¹ Pope and Heycock, *British Patent*, 142879 (1918).

² Kretov (*J. Chem. Ind. Moscow*, 1928, 5, 1268) gives d_{20}^{20} 1.6222.

³ Beckmann, *Zeitsch. physikal. Chem.*, 1909, 65, 289.

⁴ Michaelis and Schifferdecker, *Ber.*, 1872, 5, 924; 1873, 6, 996; Roozeboom and Aten, *Proc. K. Akad. Wetensch. Amsterdam*, 1904, 6, 599; Aten, *Zeitsch. physikal. Chem.*, 1905, 54, 55; Beckmann, *ibid.*, 1909, 65, 289; Ruff, *Ber.*, 1904, 37, 4513; Ruff and Fischer, *ibid.*, 1903, 36, 418.

⁵ Beckmann, *loc. cit.*; Ruff, *loc. cit.*

⁶ Ruff and Geisel, *Ber.*, 1904, 37, 1573.

but an excess of sulphur trioxide leads to simultaneous formation of pyrosulphuryl chloride :



Sulphur dioxide does not exert any action on sulphur tetrachloride, but above 0°C . chlorosulphonic acid yields the same products as those given in the first equation for the action of sulphur trioxide, whilst below 0°C . the product is sulphur oxytetrachloride, $\text{S}_2\text{O}_3\text{Cl}_4$.¹

Many chlorides, especially those of the metals, combine with sulphur tetrachloride to produce unstable crystalline additive compounds ;² thus, iodine trichloride, antimony pentachloride, titanium tetrachloride, stannic chloride, ferric chloride, and also arsenic fluoride, yield crystalline products containing the added molecule SCl_4 ; this provides strong evidence of the definite existence of this chloride of sulphur.

In its action on organo-magnesium compounds,³ sulphur tetrachloride behaves as if it consists only of sulphur dichloride and chlorine, and its reactions with sulphur trioxide (see before) appear to be capable of a similar interpretation ; in these cases it is indeed possible that sulphur dichloride and chlorine, present as products of dissociation, are the actual agents in the chemical change.

Sulphur Monobromide, or Disulphur Dibromide, S_2Br_2 .—This is the only definite bromide of sulphur. It is obtained on heating an equi-atomic mixture of sulphur and bromine at 100°C . in a sealed tube.⁴ The product is distilled under reduced pressure and collected in a dry receiver. Combination of the two elements can also occur at a lower temperature, as is shown by the fact that sulphur dissolved in bromine is present as sulphur monobromide molecules and not as free sulphur, proof being possible by cryoscopic measurements.⁵

Sulphur monobromide is also formed when sulphur monochloride and potassium bromide are heated together in a sealed tube. It is a garnet-red, oily liquid, which does not wet glass ; its density is 2.6355 at 20°C . ; its melting-point is -46°C . and its boiling-point 54°C . at 0.18 mm. ; at higher pressures the boiling-point is inconstant, due to dissociation.⁶ The refractive index, n_{7820} , is 2.6268.⁷

Sulphur monobromide is a slightly exothermic substance⁸ with respect to its elements. It is decomposed by water in an analogous manner to the monochloride, but more readily. It dissolves sulphur readily on warming, depositing some of the solid again on cooling. Yellow phosphorus dissolves in the cold liquid, but on warming explosive chemical action sets in. Iodine monochloride reacts giving iodine bromide and sulphur monochloride.

In the presence of alkali the bromide decomposes with formation of a sulphite, a bromide and sulphur :⁹



¹ Michaelis and Schifferdecker, *Annalen*, 1873, 170, 1 ; also *loc. cit.*

² Rose, *Ann. Phys. Chem.*, 1837, 42, 517 ; Ruff, *loc. cit.*

³ Ferrario, *Bull. Soc. chim.*, 1910, [iv.], 7, 518. See also Beckmann, *Zeitsch. physikal. Chem.*, 1909, 65, 289.

⁴ Gernez, *Compt. rend.*, 1876, 82, 1152 ; Ruff and Winterfeld, *Ber* 1903, 36, 2437.

⁵ Beckmann, *Sitzungsber. K. Akad. Wiss. Berlin*, 1913, p. 886 ; see also Wright, *Trans. Chem. Soc.*, 1916, 109, 1134.

⁶ Muir, *Trans. Chem. Soc.*, 1875, 28, 845 ; Hannay, *ibid.*, 1873, 26, 823.

⁷ Ruff and Winterfeld, *loc. cit.*

⁸ Michaelis, *Zeitsch. Chem.*, 1871, [ii.], 7, 185.

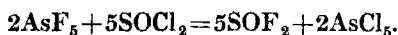
⁹ Korndörfer, *Arch. Pharm.*, 1904, 242, 156.

Existence of other Bromides.—At one time the existence of compounds SBr_2 and SBr_4 was suspected, but the evidence is insufficient and unconvincing.¹ The curves representing the vapour pressures and the freezing-points of mixtures of sulphur monobromide and bromine give no indication of the formation of any compound. The evidence thus supplied merely indicates that neither dibromide nor tetrabromide is formed on mixing the monobromide and bromine.²

Sulphur and Iodine.—Various methods have been described for the preparation of compounds of iodine and sulphur,³ but to-day the products are regarded merely as mixtures of the elements.⁴ In solution in carbon disulphide, iodine and sulphur exist side by side permanently uncombined. The freezing-point curves for mixtures of the two elements,⁵ as also the vapour pressure curve of the fusion products,⁶ likewise give no indication whatever of chemical combination, although sulphur forms a solid solution in iodine. A further proof of the absence of combination is the fact that when dissolved in iodine, sulphur has a normal molecular weight, determined cryoscopically, only a little below that required for S_8 .⁷ The present condition of our knowledge, therefore, may be summed up in the statement that no definite compound of sulphur and iodine has yet been obtained.⁸

Oxyhalides.

Thionyl Fluoride, SOF_2 .—Thionyl fluoride was first obtained pure by Moissan and Lebeau in 1900⁹ by heating a mixture of arsenic pentafluoride and thionyl chloride in a glass tube at $100^\circ C.$ for half an hour. The tube was cooled to $-80^\circ C.$ before re-opening, the liquid then being allowed to evaporate by cautiously allowing the temperature to rise, the thionyl fluoride, which boiled away at a little below $30^\circ C.$, being collected over mercury. The gas was freed from traces of thionyl chloride and arsenic pentafluoride by passage through a spiral tube at $-28^\circ C.$, the fluoride passing over uncondensed:



A modification of this method has been used by Steinkopf and Herold.¹⁰ An ice-cooled brass flask containing arsenic fluoride was fitted with a reflux condenser connected to a second condenser which led to a leaden vessel cooled to -50° or $-60^\circ C.$ The calculated quantity of thionyl

¹ Michaelis, *loc. cit.*

² Ruff and Winterfeld, *loc. cit.*; Roozeboom and Aten, *Proc. K. Akad. Wetensch. Amsterdam*, 1904, 6, 599; Muir, *loc. cit.*

³ Gay-Lussac, *Ann. Chim. Phys.*, 1813, 88, 319; Guthrie, *Trans. Chem. Soc.*, 1862, 14, 57; Menke, *Chem. News*, 1879, 39, 19; Prunier, *J. Pharm. Chim.*, 1899, [vi.], 9, 421; Lamers, *J. prakt. Chem.*, 1861, 84, 349; von Rath, *Ann. Phys. Chem.*, 1860, [ii.], 110, 116; Henry, *J. Pharm. Chim.*, 1848, 13, 403.

⁴ Sestini, *Répertoire de chimie appliquée*, 1859, 5, 401; Linebarger, *Amer. Chem. J.*, 1895, 17, 33; McLeod, *Chem. News*, 1892, 66, 111.

⁵ Smith and Carson, *Zeitsch. physikal. Chem.*, 1907, 61, 200; Ephraim, *Zeitsch. anorg. Chem.*, 1908, 58, 338; Olivari, *Atti R. Accad. Lincei*, 1908, [v.], 17, ii., 512; Boulouch, *Compt. rend.*, 1903, 136, 1577; Beckmann and Hanshan, *Zeitsch. anorg. Chem.*, 1912, 80, 221.

⁶ Wright, *Trans. Chem. Soc.*, 1915, 107, 1527.

⁷ Beckmann and Hanshan, *loc. cit.*

⁸ Amadori, *Gazzetta*, 1922, 52, i., 387; Mori, *J. Chem. Soc. Japan*, 1923, 44, 730.

⁹ Moissan and Lebeau, *Compt. rend.*, 1900, 30, 1436.

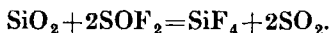
¹⁰ Steinkopf and Herold, *J. prakt. Chem.*, 1920, [ii.], 101, 79.

chloride was gradually added to the arsenic fluoride and the flask slowly warmed to about 80° C., when the thionyl fluoride distilled into the cooled lead receiver, whilst the arsenic fluoride and chloride and thionyl chloride were held back by the reflux condenser.

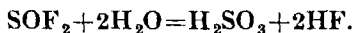
Thionyl fluoride has also been obtained in excellent yield by the interaction of liquid hydrogen fluoride and nitrogen sulphide in the presence of a little copper oxide, the reaction being best effected in a copper bomb at 100° C. The gas, which issues on opening the bomb, can be collected in a receiver cooled by liquid air.¹

The fluoride is a colourless gas which fumes in moist air and has a pungent, unpleasant odour, recalling that of carbonyl chloride. It condenses at -30° C. to a liquid which on further cooling gives a solid of m.pt. -110° C. Its vapour density corresponds with the formula SOF_2 . It is soluble in arsenic chloride, ether, benzene and turpentine.

When submitted, in a glass vessel, to the electric spark discharge, or when heated to 400° C., gradual decomposition sets in, with formation of sulphur dioxide and fluorine, the latter giving rise to silicon tetrafluoride, and the total change being representable by the equation :



When not in contact with glass, *e.g.* in a tube of platinum, thionyl fluoride can be heated to a white heat without appreciable decomposition. Water causes a slow hydrolysis :



At high temperatures hydrogen acts on the gas with formation of hydrogen fluoride, water, hydrogen sulphide and free sulphur. Chlorine in sunlight, or in contact with charcoal in a glass tube, gives rise to sulphuryl chloride and silicon fluoride. A mixture of thionyl fluoride with moist nitrogen trioxide in the presence of silica undergoes chemical change with formation of silicon fluoride and nitrosulphonic acid.²

Sulphur and phosphorus do not affect the fluoride even at 500° C., but hot sodium causes gradual decomposition, with complete absorption.

Sulphuryl Fluoride, SO_2F_2 .—This gas was obtained by Moissan and Lebeau by heating a gaseous mixture of sulphur dioxide and fluorine electrically with a platinum wire. By this method the resulting sulphuryl fluoride contains thionyl fluoride, sulphur dioxide and oxygen, the sulphur impurities being removable by water and the oxygen by cooling to -80° C., which leaves it uncondensed.

The combustion of fluorine in moist hydrogen sulphide or the interaction of fluorine and dry hydrogen sulphide in a glass vessel (the last-named supplying the necessary oxygen) also gives rise to a mixture of sulphuryl fluoride with thionyl fluoride, sulphur hexafluoride and silicon fluoride.³

Sulphuryl fluoride is a colourless, odourless gas, which liquefies at -52° C. and solidifies in liquid air, melting then at -120° C. It is remarkably stable, and dissolves unchanged in water to the extent of approximately 1 volume in 10 at the ordinary temperature; alcohol absorbs about three volumes of the gas at the ordinary temperature.

¹ Ruff and Thiel, *Ber.*, 1905, 38, 549.

² Ruff and Thiel, *loc. cit.*

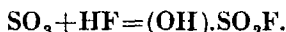
³ Moissan and Lebeau, *Compt. rend.*, 1901, 132, 374.

Chemically the gas is surprisingly inactive. It is unaffected by water at 150° C., but an aqueous solution of potassium hydroxide causes decomposition into potassium fluoride and sulphate :



It attacks glass at a red heat, giving silicon tetrafluoride and sulphur trioxide. Carbon and boron are without action on the gas at a red heat, but sodium at a temperature considerably above the melting-point causes gradual decomposition with absorption. Hydrogen sulphide, aided by heat, attacks both thionyl and sulphuryl fluorides, inducing decomposition.¹

Fluorosulphonic Acid, $\text{FSO}_2(\text{OH})$.—This was first obtained by the addition of anhydrous hydrogen fluoride to sulphur trioxide in a platinum vessel cooled in a freezing mixture, a slight excess of the halogen acid being used and removed subsequently by a current of dry carbon dioxide at about 80° C. :²



It is more conveniently prepared by dissolving ammonium fluoride in fuming sulphuric acid and heating, when fluorosulphonic acid distils ;³ metallic fluorides may also be used.

Fluorosulphonic acid is a mobile, colourless liquid, boiling at 162.6° C. ; it possesses only a slight pungent odour, and has little action on the dry skin. Distillation is accompanied by only very slight decomposition, probably into sulphuryl fluoride and sulphuric acid. Water causes vigorous decomposition ; dry glass is but slightly affected ; lead is rapidly converted into lead sulphate and fluoride, whilst with sulphur, sulphur dioxide and hydrofluoric acid are slowly produced.³

The Fluorosulphonates.—The alkali fluorosulphonates may be prepared by the action of the corresponding hydroxides upon an aqueous solution of ammonium fluorosulphonate. Ammonium fluorosulphonate is best obtained by the gradual addition of dry ammonium fluoride to sulphuric acid containing about 70 per cent. SO_3 , the product being treated with a slight excess of ammonia dissolved in methyl alcohol.⁴ Fluorosulphonates can also be obtained by heating together pyrosulphates and fluorides, either in the dry state or in the presence of a little water.⁵ Double decomposition may also be effected between fluorosulphonic acid and sodium chloride at 230° C. with formation of sodium fluorosulphonate. *Ammonium fluorosulphonate* melts at 245° C., and reacts readily with gaseous ammonia, particularly at low temperatures, forming liquid amines. *Potassium fluorosulphonate* melts at 311° C., and the *rubidium salt* at 304° C. The *lithium salt* forms long, shining needles, which contain three molecules of water of crystallisation, and melt at 60° to 61° C. In the anhydrous state the lithium salt melts at about 360° C.

The fluorosulphonates are stable towards water and may be crystallised from this solvent. In the presence of mineral acids they are readily hydrolysed to hydrofluoric and sulphuric acids. In alkaline

¹ Moissan and Lebeau, *loc. cit.*

² Thorpe and Kermann, *Trans. Chem. Soc.*, 1892, 63, 921.

³ Ruff, *Ber.*, 1914, 47, 652, 656 ; Ruff and Braun, *ibid.*, 1914, 47, 646.

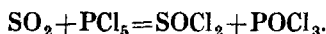
⁴ Traube, Hoerenz and Wunderlich, *ibid.*, 1919, 52, [B], 1272.

⁵ Traube, *ibid.*, 1913, 46, 2525.

solution they are much more stable. They interact with ammonium hydroxide, forming chiefly aminosulphonates. The alkali fluorosulphonates are very stable towards heat.

Thionyl Chloride, SOCl_2 .—This substance in an impure condition was first obtained by Persoz and Bloch in 1849 by the interaction of sulphur dioxide and phosphorus pentachloride. Further early investigations were made by Schiff in 1857 and by Carius between 1856 and 1864.¹

Preparation.—(1) The reaction by which the substance was discovered can be effected conveniently by passing sulphur dioxide over phosphorus pentachloride, when the resulting thionyl chloride can subsequently be separated from the accompanying phosphoryl chloride by fractional distillation :

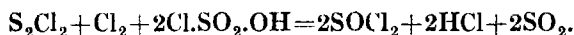


(2) Thionyl chloride can be obtained by the interaction of sulphur chlorides with sulphur trioxide : ²



It is convenient, however, to use the commoner monochloride, with which a similar reaction readily occurs at 75° to 80° C. ; the sulphur produced can be reconverted continuously into monochloride by means of a current of chlorine, and the formation of the thionyl chloride can be assisted by the addition of suitable catalysts, such as antimony trichloride or mercuric chloride.

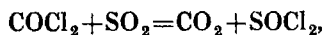
(3) Another process which may be regarded in some ways as a modification of (2) is based on the interaction of sulphur or sulphur monochloride with chlorosulphonic acid in a stream of chlorine, the same catalysts as before again being applicable : ³



(4) Other chemical changes yielding thionyl chloride include the action of phosphorus pentachloride on sulphuryl chloride,⁴ sulphites and thiosulphates ; ⁵ these processes may be regarded as modifications of (1) :



Thionyl chloride is also formed by the oxidation with chlorine monoxide of sulphur in carbon disulphide or even of carbon disulphide itself,⁶ and in the interaction of carbonyl chloride with sulphur dioxide at temperatures above 200° C.,



which reaction occurs readily if the gaseous mixture is passed over a suitable "contact" material, e.g. heated wood charcoal.⁷

¹ Persoz and Bloch, *Compt. rend.*, 1849, 28, 86 ; Schiff, *Annalen*, 1857, 102, 111 ; Carius, *ibid.*, 1858, 106, 303 ; 1859, 111, 93.

² Michaelis, *Ber.*, 1872, 5, 929 ; Béhal and Auger, *Bull. Soc. chim.*, 1888, [ii.], 50, 594.

³ Bayer & Co., *British Patent*, 27830 (1913).

⁴ Michaelis, *Ber.*, 1872, 5, 929 ; *Zeitsch. Chem.*, 1870, [ii.], 6, 460.

⁵ Carius, *loc. cit.*

⁶ Wurtz, *Compt. rend.*, 1866, 62, 460 ; Schützenberger, *ibid.*, 1868, 66, 747.

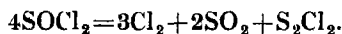
⁷ Chem. Fabr. Buckau, *German Patent*, 284935 (1914). See *J. Soc. Chem. Ind.*, 1915, 34, 1092.

The spontaneous decomposition of sulphur oxytetrachloride, $S_2O_3Cl_4$ (p. 95), also gives rise to thionyl chloride.¹

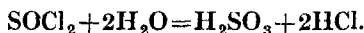
Physical Properties.—Thionyl chloride is a colourless, refractive liquid, of density 1.676 at 0° C., with freezing-point -104.5° C.² and boiling-point 79° C.,³ under atmospheric pressure. The vapour badly attacks the mucous membranes and possesses an odour recalling that of sulphur dioxide. Up to 150° C. the vapour density is normal, but above this temperature decomposition sets in, finally causing a value only two-thirds of the normal⁴ (see the following).

With respect to its elements, the substance is exothermic to the extent of approximately 47200 calories per gram-molecule; the latent heat of vaporisation is 54.45 calories per gram and the specific heat at ordinary temperatures is 0.2425.⁵ When dissolved in benzene or chloroform, thionyl chloride possesses practically a normal molecular weight,⁶ but when used as a solvent it permits ionisation.⁷ Its dielectric constant is 9.05 at 22° C.⁸

Chemical Properties.—As mentioned before, thionyl chloride is decomposed by heat, and at a dull redness it gives chlorine, sulphur dioxide and sulphur monochloride:



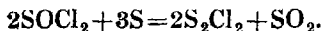
Water in the cold causes hydrolysis to sulphurous acid and hydrogen chloride, but with hot water some sulphur and sulphuric acid may also be formed:⁹



The silent electric discharge in the presence of hydrogen causes transformation of thionyl chloride into sulphur monochloride and sulphur dioxide, with hydrogen chloride:¹⁰



At 180° C. thionyl chloride converts sulphur into sulphur monochloride, with simultaneous formation of sulphur dioxide, this change in all probability being dependent on the afore-mentioned thermal decomposition:¹¹



Under similar conditions thionyl chloride reacts with both red and yellow phosphorus with formation of phosphorus trichloride according to the equation:



Prolonged heating tends to produce the pentachloride:



¹ Michaelis and Mathias, *Ber.*, 1873, 6, 1452.

² Mayes and Partington, *Trans. Chem. Soc.*, 1926, p. 2594.

³ Wurtz, *loc. cit.*; Carius, *loc. cit.*

⁴ Heumann and Köchlin, *Ber.*, 1883, 16, 1625.

⁵ Ogier, *Compt. rend.*, 1882, 94, 82.

⁶ Oddo, *Gazzetta*, 1901, [ii.], 31, 222.

⁷ Walden, *Zeitsch. anorg. Chem.*, 1900, 25, 209.

⁸ Schlundt, *J. Phys. Chem.*, 1901, 5, 503.

⁹ Carius, *loc. cit.*

¹⁰ Besson and Fournier, *Compt. rend.*, 1910, 150, 1752.

¹¹ Carius, *loc. cit.*; also Besson and Fournier, *loc. cit.*; North and Thomson, *J. Amer. Chem. Soc.*, 1918, 40, 774.

¹² North and Thomson, *loc. cit.*

At higher temperatures phosphorus trichloride reacts with thionyl chloride¹ according to the equation :



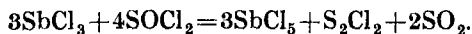
Selenium and tellurium are converted into their respective tetrachlorides by thionyl chloride, whilst gold, mercury, bismuth, arsenic, antimony, tin and iron give a mixture of the metallic chloride with sulphur dioxide and sulphur monochloride,² for example :



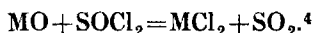
Where the metal can exist in two states of valency, as in the case of the three last-named metals, the products depend to some extent on the relative quantities of the reagents ;³ with excess of metal the course of the reaction is as follows, antimony being taken as a typical case :



whilst with an excess of thionyl chloride this reaction is followed by another :



Towards metallic oxides the behaviour of thionyl chloride is similar to that of sulphur monochloride, which is perhaps hardly surprising in view of the course of its thermal decomposition. The reaction is fairly general, the oxide being converted into the corresponding anhydrous chloride. From the action of the chloride on zinc oxide (at 150° C.), cadmium oxide (at 200° C.), arsenious oxide (up to 200° C.), antimony trioxide (at room temperature), bismuth trioxide (at 150° to 200° C.), ferric oxide (at 150° C.), magnesium oxide (at 150° to 200° C.), cupric oxide (at 200° C.) and cuprous oxide (at 200° C.), it may be concluded that the main reaction, assuming a bivalent metal, M, is as follows :



If the metal is capable of forming a higher chloride, a further reaction can occur, *e.g.* :



Calcium, strontium, aluminium and stannic oxides are not attacked.

Peroxides react vigorously with thionyl chloride, forming sulphuryl chloride. The metal remains either as chloride or as a mixture of chloride and sulphate, according to the proportion of thionyl chloride. With thionyl chloride in excess the reaction takes place according to the equation (using barium peroxide) :



whilst with excess of barium peroxide the reaction is :



¹ Michaelis, *Zeitsch. Chem.*, 1870, [u.], 6, 460.

² Heumann and Köchlin, *Ber.*, 1883, 16, 1625.

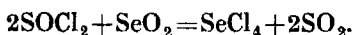
³ North, *J. Amer. Chem. Soc.*, 1912, 34, 890; North and Hageman, *ibid.*, 1910, 32, 184; North and Conover, *Chem. News*, 1916, 113, 140.

⁴ North and Hageman, *J. Amer. Chem. Soc.*, 1913, 35, 352.

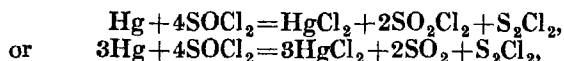
Thionyl chloride has little action on selenium at room temperature, but on heating gives the tetrachloride :



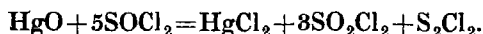
With selenium dioxide the reaction is : ¹



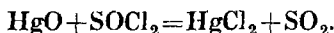
With tellurium or tellurium dioxide, thionyl chloride gives tellurium tetrachloride if SOCl_2 is in excess, or the dichloride if the element or its dioxide is in excess.² With mercury at 150°C . in a sealed tube the reaction may either be



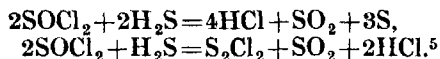
according to the proportions used.³ With mercuric oxide in a sealed tube at 160°C . and thionyl chloride in excess, the reaction is :



If the SOCl_2 is not in excess, the reaction is probably : ⁴



Hydrogen sulphide is gradually oxidised by thionyl chloride, the process being greatly accelerated by the presence of aluminium chloride ; the products are sulphur dioxide, sulphur and hydrogen chloride, together with sulphur monochloride if the thionyl chloride is in excess :



When heated in a sealed tube with thionyl chloride at 150° to 200°C ., many metallic sulphides in a similar manner yield the metallic chloride, together with sulphur monochloride and sulphur dioxide : ⁶



Most mineral sulphides may be decomposed by this means, a few hours' heating being sufficient in the case of easily decomposed sulphides such as pyrites, cinnabar, galena, orpiment, mispickel and stibnite. Pyrargyrite, proustite, covellite, sphalerite and tetrahedrite require from one to two days, whilst argentite, molybdenite and cobaltite are not attacked by thionyl chloride under these conditions.⁷

Pure sulphuric acid gradually yields chlorosulphonic acid and pyro-sulphuryl chloride by concurrent independent reactions on treatment with thionyl chloride.⁸ Nitric acid vigorously oxidises thionyl chloride to sulphuric acid, probably with intermediate formation of nitryl chloride,

¹ Lenher and North, *J. Amer. Chem. Soc.*, 1907, 29, 33.

² Lenher and Hill, *ibid.*, 1908, 30, 737.

³ North, *ibid.*, 1910, 32, 184.

⁴ North, *loc. cit.*

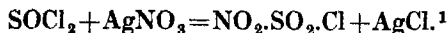
⁵ Besson, *Compt. rend.*, 1896, 123, 884 ; 122, 320.

⁶ North and Conover, *J. Amer. Chem. Soc.*, 1915, 37, 2486.

⁷ North and Conover, *Amer. J. Sci.*, 1915, [iv.], 40, 640.

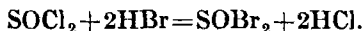
⁸ Moureu, *Compt. rend.*, 1894, 119, 337.

NO_2Cl . In the absence of moisture silver nitrate yields nitrosulphonyl chloride :



As suggested by its behaviour towards sulphuric and nitric acids, thionyl chloride is of value as a reagent for the replacement of hydroxyl groups by chlorine, and amongst the organic compounds it finds frequent application instead of the commoner chlorides or oxychloride of phosphorus.²

Even at the ordinary temperature hydrogen iodide is readily decomposed by thionyl chloride, giving hydrogen chloride, iodine, sulphur and sulphur dioxide, but hydrogen bromide undergoes a double decomposition with formation of thionyl bromide and hydrogen chloride :³



Thionyl chloride reacts with ammonia giving rise to various complex products, the nature of which varies with the conditions.⁴ With amino-sulphonic acid at 100°C . ammonium chlorosulphonate is formed.⁵

The constitution of thionyl chloride, judged by the various methods by which the substance can be prepared, can hardly be other than

$\text{O}=\text{S} \begin{array}{l} \diagup \text{Cl} \\ \diagdown \text{Cl} \end{array}$, and this view is confirmed by the formation of sulphoxides

when the substance interacts with organo-magnesium compounds,⁶ magnesium phenyl bromide, for example, yielding diphenyl sulphoxide, $(\text{C}_6\text{H}_5)_2\text{S} : \text{O}$. On account of the relationship of thionyl chloride to sulphurous acid, the molecular structure of the chloride possesses peculiar interest.

Sulphuryl Chloride, SO_2Cl_2 .—As would be expected, it is possible to obtain an acid chloride, SO_2Cl_2 , corresponding with sulphuric acid, $\text{SO}_2(\text{OH})_2$, but the chloride cannot be prepared by the action of phosphorus pentachloride on sulphuric acid or sulphur trioxide, these reagents yielding pyrosulphuryl chloride.⁷

Formation and Preparation.—Chlorine and sulphur dioxide will only unite under some accelerating influence. It was by the interaction of these gases in sunlight that sulphuryl chloride was first obtained by Regnault in 1838.

Bone charcoal or activated wood charcoal is a convenient accelerator, combination occurring instantly. If the vessel in which the reaction is carried out is cooled to 30°C ., the sulphuryl chloride is condensed and may be drained away as rapidly as it is formed.⁸ The terpene

¹ Thorpe, *Trans. Chem. Soc.*, 1882, 41, 297.

² Carius, *loc. cit.*; Denham and Woodhouse, *Trans. Chem. Soc.*, 1913, 103, 1861; Darzens, *Compt. rend.*, 1911, 152, 1314, 1601; McKenzie and Barrow, *Trans. Chem. Soc.*, 1911, 99, 1910; Green, *ibid.*, 1924, 125, 1450; 1926, p. 2198; Majima and Simanuki, *Proc. Imp. Acad. Tokyo*, 1926, 2, 544; Meyer and Graf, *Ber.*, 1928, 61, [B], 2202.

³ Besson, *loc. cit.*

⁴ Michaelis, *loc. cit.*; Schiff, *loc. cit.*; Ephraim and Piotrowski, *Ber.*, 1911, 44, 379.

⁵ Ephraim and Gurewitsch, *ibid.*, 1910, 43, 138.

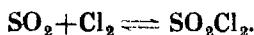
⁶ Strecker, *ibid.*, 1910, 43, 1131; Grignard and Zorn, *Compt. rend.*, 1910, 150, 1177; Oddo, *Gazzetta*, 1911, 41, i., 11.

⁷ Michaelis, *Jena. Zeitsch. Med. Naturw.*, 1870, 6, 235, 292; compare Williamson, *Annalen*, 1854, 92, 242; Carius, *ibid.*, 1858, 106, 291; Schiff, *ibid.*, 1857, 102, 111.

⁸ Pope, *Rec. Trav. chim.*, 1923, 42, 939; also *Trans. Chem. Soc.*, 1920, 117, 1410. See also McKee and Salls, *Ind. Eng. Chem.*, 1924, 16, 279; *Canadian Patent*, 251586 (1924); Danneel, *Zeitsch. angew. Chem.*, 1926, 39, 1553.

hydrocarbons, especially pinene and limonene, also certain ethers, phenols and esters, are effective catalysts, as also is camphor.¹

The formation of sulphuryl chloride is favoured by low temperature and its decomposition by high temperature :

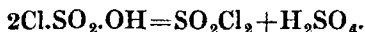


Both these reactions are catalysed by the foregoing catalysts. For the efficient preparation of the chloride, the dry reacting gases are brought together at ordinary temperatures in the presence of a catalyst such as "Norit," a highly activated powdered carbon. The mixture is then cooled to -10°C . to ensure complete combination, filtered from the catalyst and carefully distilled, the heat being applied to the liquid for as short a time as possible.²

At 120°C . in a sealed tube boron trichloride and sulphur trioxide react with formation of sulphuryl chloride :³



A convenient method for the laboratory preparation of sulphuryl chloride consists in boiling chlorosulphonic acid with about one per cent. of mercury or mercuric sulphate under a reflux condenser kept at a temperature of 70°C . in order to return to the flask any unchanged chlorosulphonic acid :



Any unchanged chlorosulphonic acid in the distillate can be removed by making use of its much more rapid hydrolysis with ice-cold water, the residual liquid being dried and redistilled.⁴

Physical Properties.—Sulphuryl chloride is a colourless, fuming liquid, with an extremely pungent odour. $D_4^{20} = 1.6674$; $n_D^{20} = 1.4437$. It boils at 69.1°C . at 760 mm. pressure, and freezes at -46°C .⁵ The vapour density is normal at first, but when the chloride is kept, even at 100°C ., its vapour commences to dissociate into sulphur dioxide and chlorine. At 200°C . dissociation is almost complete.⁶ When dissolved in benzene the substance shows a molecular weight corresponding with SO_2Cl_2 . At ordinary temperatures the specific heat is 0.288, the latent heat of evaporation 52.4 calories per gram, and the heat of formation from the elements approximately 89,540 calories per gram-molecule.⁷ The dielectric constant at 20°C . is 8.5.⁸ As a solvent, the ebullioscopic constant of sulphuryl chloride has been found to have

¹ Boake, Roberts & Co., Ltd., and Durrans, *British Patent*, 124542 (1918); Durrans, *J. Soc. Chem. Ind.*, 1926, 45, 347 T; also Cusmano, *Atti R. Accad. Lincei*, 1918, [v.], 27, ii., 201; *Gazzetta*, 1925, 55, 218.

² Terlinck, *Chem. Zeit.*, 1928, 52, 901, 944.

³ Gustavson, *Ber.*, 1873, 6, 9.

⁴ Bert, *Bull. Soc. chim.*, 1922, [iv.], 31, 1264; Ruff, *Ber.*, 1901, 34, 3509.

⁵ Pawlewski, *Ber.*, 1897, 30, 765; Behrend, *J. prakt. Chem.*, 1877, [ii.], 15, 23; Ogier, *Compt. rend.*, 1882, 94, 82. For general physical properties, see Walden, *Zeitsch. anorg. Chem.*, 1900, 25, 209; Beckmann, *ibid.*, 1912, 77, 90.

⁶ Heumann and Köchlin, *Ber.*, 1885, 16, 602. The effect of subjecting the system $\text{SO}_2\text{Cl}_2 \rightleftharpoons \text{SO}_2 + \text{Cl}_2$ to the action of light rays of different wave-lengths—absorbed only by one or other of the components—has been investigated by Le Blanc, Andrich and Kangro, *Zeitsch. Elektrochem.*, 1919, 25, 229.

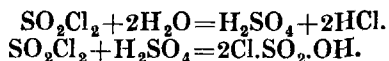
⁷ Ogier, *loc. cit.*; Thomsen, *Ber.*, 1883, 16, 2613.

⁸ Schlundt, *J. Physical Chem.*, 1901, 5, 503.

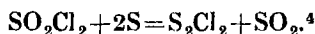
the value 45; salts dissolved in the chloride are found to undergo ionic dissociation.¹

Chemical Properties.—At a dull red heat sulphuryl chloride vapour is completely decomposed into sulphur dioxide and chlorine. At 320° C. the reaction appears to be of the first order, proceeding entirely in the gas phase; at lower temperatures, however, reaction takes place on the wall of the containing vessel.²

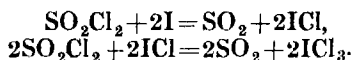
Water causes sulphuryl chloride to decompose into sulphuric and hydrochloric acids,³ but with only very little water, or better, with sulphuric acid, chlorosulphonic acid is obtained:



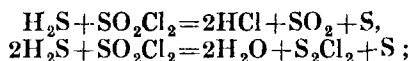
At 200° C. sulphuryl chloride converts sulphur into monochloride, this result probably being preceded by dissociation of the sulphuryl chloride into chlorine and sulphur dioxide. In the presence of aluminium chloride this reaction can be effected even at the ordinary temperature, and aluminium chloride is known to favour the dissociation of sulphuryl chloride:



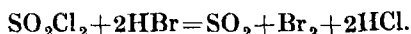
In the presence of aluminium chloride, iodine also reacts easily with sulphuryl chloride:⁵



Hydrogen sulphide is attacked according to the equations:



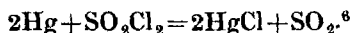
whilst hydrogen bromide and hydrogen iodide are acted upon vigorously with formation of sulphur dioxide and the free halogen:



Phosphorus (red more readily than yellow), arsenic, antimony, mercury, iron, gold and platinum are converted into chlorides, with liberation of sulphur dioxide, *e.g.*



with the mercury in excess:



In ether solution sulphuryl chloride reacts with zinc, giving zinc chloride and zinc sulfoxylate, ZnSO_2 .

¹ Walden, *loc. cit.*; Beckmann, *loc. cit.*

² Smith, *J. Amer. Chem. Soc.*, 1925, 47, 1862; cf. Hinshelwood and Prichard, *Trans. Chem. Soc.*, 1923, 123, 2727.

³ Thomsen, *Ber.*, 1883, 16, 2613; Carrara, *Gazzetta*, 1901, 31, i., 450. Baeyer and Villiger (*Ber.*, 1901, 34, 736) have described a hydrate $\text{SO}_2\text{Cl}_2.15\text{H}_2\text{O}$, the existence of which, however, is doubtful.

⁴ Ruff, *Ber.*, 1901, 34, 1749; 1902, 35, 4453; North and Thomson, *J. Amer. Chem. Soc.*, 1918, 40, 774.

⁵ Ruff, *loc. cit.*

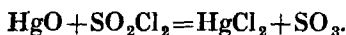
⁶ North, *Bull. Soc. chim.*, 1911, [iv.], 9, 646.

Phosphorus pentachloride effects a gradual removal of one atom of oxygen from sulphuryl chloride, with formation of thionyl chloride,



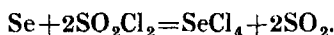
whilst phosphorus trichloride yields the same products, excepting chlorine.

Lead dioxide is converted vigorously into lead chloride and sulphate by the vapour of sulphuryl chloride, oxygen being liberated, whilst mercuric oxide (red at 160° to 180° C., yellow at 150° C.) with excess of sulphuryl chloride gives mercuric chloride and sulphur trioxide :

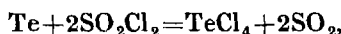


With excess of mercuric oxide, mercuric sulphate is also formed.¹

Selenium is attacked rapidly by sulphuryl chloride :



The chloride has no action on selenium dioxide even at high temperatures or under great pressure.² Sulphuryl chloride reacts with tellurium ; with the sulphuryl chloride in excess the reaction is :



whilst with the tellurium in excess, TeCl_2 is obtained. Tellurium dioxide is not acted upon in the cold, but when heated in a sealed tube with the chloride a variety of crystalline products may be formed : $3\text{TeO}_2 \cdot 4\text{SO}_2\text{Cl}_2$, $5\text{TeO}_2 \cdot 9\text{SO}_2\text{Cl}_2$, $\text{TeO}_2 \cdot 2\text{SO}_2\text{Cl}_2$, and $2\text{TeO}_2 \cdot 5\text{SO}_2\text{Cl}_2$.

The reaction between sulphuryl chloride and ammonia is complex, various products being obtained under different conditions ; the products include iminosulphamide, $\text{NH}_2 \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{SO}_2 \cdot \text{NH}_2$, which behaves as a monobasic acid, trisulphimide and sulphomelide, both acidic substances of composition $(\text{SO}_2 \cdot \text{NH})_3$, and sulphamide, $\text{SO}_2(\text{NH}_2)_2$, which is also acidic.³

Like thionyl chloride, sulphuryl chloride is able to replace the hydroxyl groups of organic substances by chlorine.⁴

Constitution.—In view of the possibility of sexavalent sulphur, as demonstrated by the existence of sulphur hexafluoride, there is very

little difficulty in accepting the formula $\begin{array}{c} \text{O} \\ \diagup \\ \text{S} \\ \diagdown \\ \text{O} \end{array} \begin{array}{c} \text{Cl} \\ \diagup \\ \text{S} \\ \diagdown \\ \text{Cl} \end{array}$ for sulphuryl chloride.

Sulphur Oxytetrachloride, $\text{S}_2\text{O}_3\text{Cl}_4$.—During the preparation of sulphur monochloride, Millon⁵ in 1838 obtained a substance which he described as a crystalline sulphur chloride ; its formation was due to the presence of moisture during the action, and similar crystals can be formed by introducing a little sulphur monochloride into a flask filled with moist chlorine. The composition of the crystals has since been shown to be represented by $\text{S}_2\text{O}_3\text{Cl}_4$.

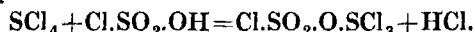
¹ North, *J. Amer. Chem. Soc.*, 1910, 32, 184. ² Lenher and North, *ibid.*, 1907, 29, 33.

³ Regnault, *Ann. Chim. Phys.*, 1838, 69, 170 ; Hantzsch and others, *Ber.*, 1901, 34, 3430 ; 1905, 38, 1022 ; Ephraim and Michel, *ibid.*, 1909, 42, 3833 ; Ruff, *ibid.*, 1903, 36, 2900.

⁴ Silberrad and Boake, Roberts & Co., Ltd., *British Patent*, 259329 (1925) ; *Trans. Chem. Soc.*, 1922, 121, 1015 ; 1925, 127, 2677 ; Durrans, *ibid.*, 1923, 123, 1424 ; Naik and Shah, *J. Ind. Chem. Soc.*, 1927, 4, 11 ; Baumgarten, *Ber.*, 1927, 60, [B], 1174.

⁵ Millon, *Compt. rend.*, 1838, 6, 207.

A more convenient method of preparation ¹ is to pass chlorine into a mixture of sulphur monochloride with a bimolecular proportion of chlorosulphonic acid at $-15^{\circ}\text{C}.$, until solidification occurs. Probably sulphur tetrachloride is first formed and then reacts with the chlorosulphonic acid :



Sulphur oxytetrachloride ¹ is a pungent, colourless, crystalline solid of m.pt. $57^{\circ}\text{C}.$, with decomposition. Even when kept at the ordinary temperature it gradually liquefies on account of decomposition into thionyl and sulphuryl chlorides; if decomposed rapidly at higher temperatures, the latter compound is naturally accompanied by or even replaced by its dissociation products.²



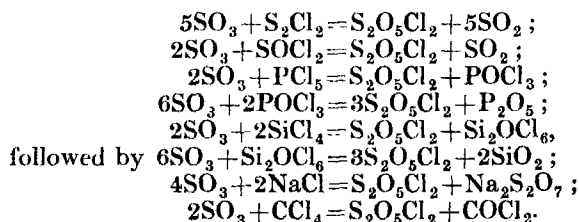
Treatment with water causes hydrolysis to sulphuric and sulphurous acids, together with hydrochloric acid :



Sulphuric acid reacts with sulphur oxytetrachloride as with sulphuryl chloride, yielding chlorosulphonic acid.

In accordance with its reactions the constitution of sulphur oxytetrachloride must be regarded as represented by $\text{Cl}.\text{SO}_2.\text{O}.\text{SCl}_3$.³

Pyrosulphuryl Chloride, $\text{S}_2\text{O}_5\text{Cl}_2$.—Rose first prepared this substance in 1838 by the interaction of sulphur trioxide and sulphur monochloride.⁴ It is formed by the action of many chlorides on sulphur trioxide; sulphur monochloride,⁴ thionyl chloride,⁵ silicon tetrachloride,⁶ phosphorus pentachloride,⁷ phosphorus oxychloride,⁸ sodium chloride⁹ and carbon tetrachloride¹⁰ all yield the desired product when treated with sulphur trioxide at a suitable temperature. With sodium chloride a mixture of pyrosulphuryl chloride and sodium pyrosulphate is obtained, whilst with the exception of carbon tetrachloride and phosphorus pentachloride, which are converted into oxychlorides, all the remaining chlorides are changed into oxides



¹ Michaelis and Schifferdeckér, *Ber.*, 1873, 6, 996, *Annalen*, 1873, 170, 22.

² Michaelis and Mathias, *Ber.*, 1873, 6, 1452.

³ Ogier (*Compt. rend.*, 1882, 94, 446) described a substance as an oxytetrachloride of the formula S_2OCl_4 , but it has been shown by Knoll (*Ber.*, 1898, 31, 2183) that this product was in all probability a mixture of sulphuryl, thionyl and sulphur chlorides.

⁴ Rose, *Ann. Phys. Chem.*, 1838, 44, 291.

⁵ Michaelis, *Zeitsch. Chem. Phys. Math.*, 1871, 7, 149.

⁶ Gustavson, *Ber.*, 1872, 5, 332, Sanger and Riegel, *Zeitsch. anorg. Chem.*, 1913, 80, 252.

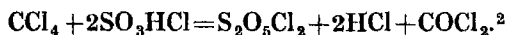
⁷ Michaelis, *loc. cit.*

⁸ Rose, *loc. cit.*

⁹ Rosenstiehl, *Compt. rend.*, 1861, 53, 658.

¹⁰ Armstrong, *J. prakt. Chem.*, 1870, [n.], 1, 244; Schützenberger, *Compt. rend.*, 1869, 69, 352; Prud'homme, *Bull. Soc. chim.*, 1870, 14, 385; Sanger and Riegel, *Zeitsch. anorg. Chem.*, 1912, 76, 79; Prandtl and Borinski, *ibid.*, 1909, 62, 24, 237.

The most convenient process is to add a mixture of sulphur trioxide and fuming sulphuric acid gradually to hot carbon tetrachloride, the product being purified by fractional distillation, followed by treatment with sodium chloride to remove any chlorosulphonic acid and subsequent redistillation,¹ preferably under reduced pressure. Fuming sulphuric acid reacts with carbon tetrachloride at 150° C. with formation of chlorosulphonic acid and carbonyl chloride. The chlorosulphonic acid then reacts with more carbon tetrachloride thus :

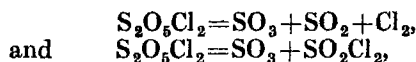


When chlorosulphonic acid is dehydrated by the action of phosphorus pentoxide³ or pentachloride,⁴ pyrosulphuryl chloride is obtained :

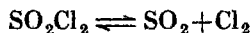


Pyrosulphuryl chloride is a colourless, rather viscous liquid, which in the air fumes less strongly than sulphur trioxide. It boils at 152° to 152.5° C. under 766 mm. pressure, at 57° C. under 30 mm., and at 52° C. under 15 mm., without appreciable decomposition if dry.⁵ $D_4^0 = 1.872$, $D_4^{20} = 1.837$; m.pt. = -37.5° to -37° C.; $n_D^{19} = 1.449$. From vapour density determinations it is known that at 180° C. the molecular weight is normal⁵ but that at higher temperatures decomposition occurs. The liquid chloride is exothermic with respect to its elements, the heat of formation, according to Ogier,⁶ being 159,400 calories, but according to Konowalov⁷ 188,200 calories. The specific heat of the liquid is 0.258, and the molecular heat of vaporisation according to the last-named investigator is 7550 calories, a figure more in accordance with Trouton's Rule than the high value of 13,160 calories given by Ogier.

When passed through a red-hot tube the vapour is almost entirely decomposed into sulphur dioxide, sulphur trioxide and chlorine. Vapour density determinations at various temperatures, and analyses of the decomposition products, indicate that decomposition proceeds according to the equations :⁸



the former reaction occurring to a small extent at 200° C. in the presence of sulphur dioxide and chlorine, but giving place at higher temperatures to the second reaction, when



follows and decomposition is complete at 360° C.

¹ Sanger and Riegel, *loc. cit.*

² Manguin and Simon, *Compt. rend.*, 1919, 169, 34; also Lepin, *J. Russ. Phys. Chem. Soc.*, 1920, 52, 1; Grignard and Muret, *Compt. rend.*, 1926, 183, 581.

³ Billitz and Houmann, *Ber.*, 1883, 16, 483; Konowalov, *Compt. rend.*, 1882, 95, 1284.

⁴ Michaelis, *loc. cit.*

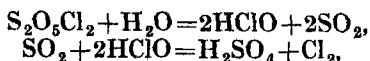
⁵ Konowalov, *loc. cit.*; Besson, *Compt. rend.*, 1897, 124, 401; Sanger and Riegel, *loc. cit.*; Prandtl and Borinski, *loc. cit.*; Grignard and Muret, *loc. cit.*

⁶ Ogier, *Compt. rend.*, 1882, 94, 82.

⁷ Konowalov, *Ber.*, 1883, 16, 2629; *Compt. rend.*, 1882, 95, 1284.

⁸ Grignard and Muret, *loc. cit.*

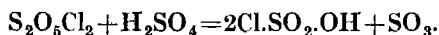
The liquid chloride is only gradually attacked by water, giving sulphuric and hydrochloric acids, but if the relative quantity of water is very small, two reactions occur,¹



such solutions having oxidising properties.

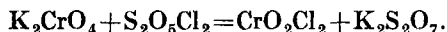
Like sulphuryl chloride, pyrosulphuryl chloride can convert many elements, *e.g.* sulphur, phosphorus, antimony and mercury, into the corresponding chlorides, with simultaneous formation of sulphur dioxide and trioxide.² In the reaction between pyrosulphuryl chloride and phosphorus pentachloride or trichloride, there are obtained phosphorus oxychloride, sulphur dioxide and chlorine.

Pyrosulphuryl chloride is not miscible with sulphuric acid, but when sealed together in a tube the two liquids become homogeneous in the course of a few weeks, the sulphuric acid undergoing dehydration :³



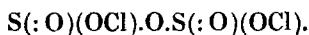
Hydrogen bromide, iodide and sulphide are oxidised to the corresponding elements, various reduction and hydrolytic products of the pyrosulphuryl chloride being formed at the same time. Phosphine also causes reduction of pyrosulphuryl chloride with production of sulphide of phosphorus.⁴

With chromates, chromyl chloride is produced :⁵



Selenium is oxidised to a selenium sulphur oxytetrachloride.⁶

From the chemical behaviour of the substance and especially its relationship to chlorosulphonic acid, it is evident that pyrosulphuryl chloride may be regarded as chlorosulphonic anhydride, $\text{Cl}.\text{SO}_2.\text{O}.\text{SO}_2.\text{Cl}$. Grignard and Muret consider that the properties of the compound are best accounted for by the formula



Chlorosulphonic Acid, $\text{Cl}.\text{SO}_2.\text{OH}$.—In 1854 the discovery of chlorosulphonic acid by Williamson, by the interaction of hydrogen chloride and sulphur trioxide, was of especial interest. Ideas of valency were immature and undeveloped, and for the systematisation of the knowledge of organic and inorganic compounds reference was made to

various *types* such as HCl , $\left. \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \right\} \text{O}$ and $\left. \begin{smallmatrix} \text{H} \\ \text{H} \\ \text{H} \end{smallmatrix} \right\} \text{N}$, from which other sub-

stances could be regarded as derived by substitution of one or more of the hydrogen atoms by other atoms or groups of atoms. Chlorosulphonic acid was the first example of a compound derived simultaneously from two types, namely from hydrogen chloride and water by the replacement of a hydrogen atom from each by the group SO_2 .

¹ Grignard and Muret, *Compt. rend.*, 1926, 183, 713.

² Heumann and Kochlin, *Ber.*, 1883, 16, 479; Besson, *loc. cit.*; Prandtl and Borinski, *loc. cit.*

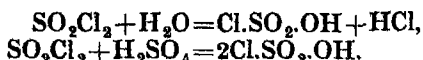
³ Sanger and Riegel, *loc. cit.*

⁴ Besson, *loc. cit.*

⁵ Clausnizer, *Ber.*, 1878, 11, 2010.

⁶ Rosenstiehl, *Compt. rend.*, 1861, 53, 658.

The following methods are available for the preparation of chloro-sulphonic acid : (1) The substance can be obtained by the gradual action of moisture (*e.g.* atmospheric moisture) on sulphuryl chloride ; a similar reaction occurs with sulphuric acid and is more easily regulated :



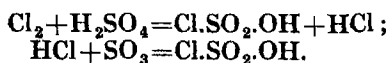
To the former reaction is also to be ascribed the formation of chloro-sulphonic acid when moist chlorine and sulphur dioxide are passed over platinum at a red heat.¹

(2) Concentrated or fuming sulphuric acid also gives rise to chloro-sulphonic acid when treated with phosphorus pentachloride :²



other acid chlorides such as phosphorus oxychloride,³ phosphorus trichloride,⁴ sulphuryl chloride (see before), pyrosulphuryl chloride,⁵ sulphur oxytetrachloride,⁶ and even sulphur monochloride,⁷ give a similar result.

(3) Even chlorine alone will act on sulphuric acid, giving chloro-sulphonic acid,⁷ as also will hydrogen chloride on sulphur trioxide⁸ or on a mixture of sulphuric acid and phosphorus pentoxide.⁹ Indeed, the interaction of hydrogen chloride and sulphur trioxide in the presence of sulphuric acid provides the most convenient method for preparing chlorosulphonic acid, the product being purified by distillation in an atmosphere of hydrogen chloride, followed by fractional crystallisation :¹⁰



Chlorosulphonic acid is a colourless fuming liquid of sharp, unpleasant odour. It boils at 151° to 152·5° C. at 765 mm., or at 74° to 75° C. at 19 mm., and it melts at -81° to -80° C.; $D_4^0 = 1\cdot784$, $D_4^{20} = 1\cdot753$.¹¹ At the boiling-point the vapour density is normal, but marked dissociation occurs at higher temperatures, *e.g.* at 200° C., with formation of sulphur trioxide and hydrogen chloride.¹² Referred to solid sulphur trioxide and gaseous hydrogen chloride, the formation of chloro-sulphonic acid is exothermic to the extent of 14·4 Calories per gram-molecule ; the specific heat at ordinary temperatures is 0·282 and the latent heat of vaporisation 12·8 Calories per gram-molecule.¹³

When heated strongly, the vapour of chlorosulphonic acid undergoes decomposition into sulphur trioxide and hydrogen chloride¹⁴ or, at

¹ Railton, *Trans. Chem. Soc.*, 1869, 7, ii., 183.

² Williamson, *Proc. Roy. Soc.*, 1856, 7, 11 ; 1861, 53, 658.

³ Michaelis, *Zeitsch. Chem. Phys. Math.*, 1871, 7, ii., 149.

⁴ Geuther, *Ber.*, 1872, 5, 925.

⁵ Sanger and Riegel, *loc. cit.*

⁶ Billitz and Heumann, *Ber.*, 1883, 16, 602.

⁷ Beckurtz and Otto, *ibid.*, 1872, 5, 925 ; 1878, 11, 2058 ; Behrend, *ibid.*, 1875, 8, 1004 ; Müller, *ibid.*, 1873, 6, 227 ; Williams, *Trans. Chem. Soc.*, 1869, 22, ii., 304.

⁸ Williamson, *loc. cit.*

⁹ Müller, *loc. cit.*

¹⁰ Sanger and Riegel, *Zeitsch. anorg. Chem.*, 1912, 76, 79.

¹¹ Sanger and Riegel, *loc. cit.* See also Michaelis, *loc. cit.*

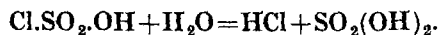
¹² Heumann and Köchlin, *Ber.*, 1882, 15, 416 ; 1883, 16, 602 ; Baumstark, *Annalen*, 1886, 140, 75.

¹³ Ogier, *Compt. rend.*, 1883, 96, 646.

¹⁴ Williamson, *Trans. Chem. Soc.*, 1869, 7, ii., 304.

higher temperatures, into sulphur dioxide, sulphuric acid and chlorine; ¹ under suitable conditions, *e.g.* at 180° to 210° C. in a sealed tube or especially readily in the presence of certain catalysts ² such as mercury or mercuric chloride, platinum chloride, copper, iodine or sulphur, the liquid substance undergoes disruption into sulphuryl chloride and sulphuric acid.³

Water causes very vigorous hydrolysis to sulphuric acid and hydrogen chloride, the action being much more rapid than with pyrosulphuryl chloride: ⁴



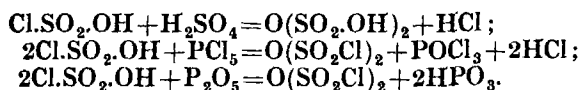
Hydrogen sulphide is readily decomposed by chlorosulphonic acid with formation of sulphur, sulphur monochloride and sulphuric acid; ⁵ the reaction may be expressed as



but is probably more complex.

Chlorosulphonic acid possesses a strong chlorinating power and converts sulphur, phosphorus, arsenic, antimony and tin into the corresponding chlorides, sulphur dioxide together with sulphuric and hydrochloric acids being simultaneously produced.⁶ With sulphur and with yellow phosphorus interaction occurs at the ordinary temperature, often becoming uncontrollable with the latter element.

With sulphuric acid and phosphorus pentachloride, respectively, fuming sulphuric acid and pyrosulphuryl chloride are obtained; ⁷ in the latter case the effect is one of dehydration, and a similar result is producible with phosphorus pentoxide: ⁸



Potassium sulphate, when warmed with chlorosulphonic acid, yields *potassium pyrosulphate*,⁹ the reaction being analogous to that of sulphuric acid with the chloro-acid; silver nitrate is vigorously converted into silver chloride, with concurrent formation of nitrosulphonic acid.¹⁰

At the ordinary temperature chlorosulphonic acid dissolves sodium chloride, displacing hydrogen chloride and forming sodium chlorosulphonate,¹¹ this reaction being due to its acidic nature. It is of interest that *ammonium chlorosulphonate* can be synthesised by the action of sulphuryl chloride on aminosulphonic acid at 100° C.¹²

¹ Clausnizer, *loc. cit.*; Beckurtz and Otto, *loc. cit.*

² Ruff, *Ber.*, 1901, 34, 3509.

³ Behrend, *ibid.*, 1875, 8, 1004.

⁴ For the use of this reaction in the determination of chlorosulphonic acid, see Weissenberger and Zoder, *Zeitsch. anal. Chem.*, 1922, 61, 41; Mayr, *Zeitsch. anorg. Chem.*, 1924, 136, 238.

⁵ Prinz, *Annalen*, 1884, 223, 371.

⁶ Heumann and Köchlin, *loc. cit.*

⁷ Michaelis, *loc. cit.*

⁸ Billitz and Heumann, *Ber.*, 1883, 16, 482; Konowalov, *Compt. rend.*, 1883, 96, 1146.

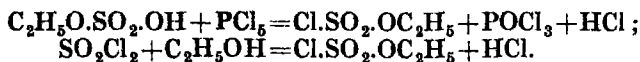
⁹ Schiff, *Annalen*, 1863, 126, 167.

¹⁰ Thorpe, *Trans. Chem. Soc.*, 1882, 41, 297.

¹¹ Müller, *Ber.*, 1873, 6, 227.

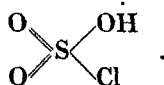
¹² Ephraim and Gurewitsch, *ibid.*, 1910, 43, 138.

The simple acidic nature of chlorosulphonic acid is also manifested in the existence of corresponding ethereal salts, the *ethyl ester* $\text{Cl}.\text{SO}_2.\text{OC}_2\text{H}_5$ being obtainable indirectly by the action of phosphorus pentachloride on ethyl hydrogen sulphate (ethylsulphuric acid), $\text{C}_2\text{H}_5\text{O}.\text{SO}_2.\text{OH}$, or by the interaction of sulphuryl chloride and ethyl alcohol : ¹

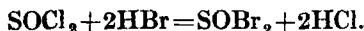


From its general behaviour it is clear that chlorosulphonic acid is closely related to sulphuric acid. Like the latter acid, but with more vigour, it attacks aromatic hydrocarbons with formation of organic *sulphonic acids* of the structure $\text{R}.\text{SO}_2.\text{OH}$ and *sulphones* of the structure

$\begin{array}{c} \text{R} \\ \diagdown \\ \text{SO}_2 \\ \diagup \\ \text{R} \end{array}$, where R represents an aromatic organic radical such as phenyl (C_6H_5) .² From these and other reactions the conclusion may be drawn that in chlorosulphonic acid the chlorine atom must be directly attached to sulphur, and therefore that the constitution must be represented as

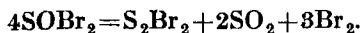


Thionyl Bromide, SOBr_2 .—This analogue of thionyl chloride is best prepared by the prolonged action of hydrogen bromide on thionyl chloride : ³



Sodium bromide or aluminium bromide may be used instead of hydrogen bromide.⁴

It is an orange-yellow liquid, density 2.697 at 15° C., b.pt. 45° C. at 22 mm., 68° C. at 40 mm., and 138° C. (with decomposition) at 773 mm. It decomposes slowly at the ordinary temperature, more rapidly on heating, yielding sulphur monobromide, sulphur dioxide and free bromine :



It is readily hydrolysed by water. It reacts with organic acids to form acid bromides. Mercury decomposes the vapour with formation of sulphur dioxide.

The liquid appears to contain associated molecules, as the following data indicate : molecular weight, 234 to 246 ; surface tension, 43.71 dynes per cm. at 17° C. ; Trouton coefficient, 25.2.

Besson,⁵ when preparing thionyl bromide by the action of boiling thionyl chloride on hydrogen bromide or aluminium bromide, claimed to have isolated the intermediate compound, *thionyl chlorobromide*, SOClBr , a more volatile liquid than thionyl bromide and therefore separated from it by distillation under reduced pressure. The product isolated was a yellow liquid, density 2.31 at 0° C., boiling with slight

¹ Bushong, *Amer. Chem. J.*, 1903, 30, 212.

² Müller, *loc. cit.* ; de Purgold, *Ber.*, 1873, 6, 502 ; Claesson, *J. prakt. Chem.*, 1879, [ii], 19, 231 ; Baumstark, *loc. cit.*

³ Mayes and Partington, *J. Chem. Soc.*, 1926, p. 2594.

⁴ Hartog and Sims, *Chem. News*, 1893, 67, 82.

⁵ Besson, *Compt. rend.*, 1896, 122, 320 ; 123, 884.

decomposition at 115° C. Mayes and Partington,¹ however, could obtain no evidence of such an intermediate compound in the product from the bromination of thionyl chloride. The physical properties of the product were similar to those of a mixture of thionyl chloride and thionyl bromide. Moreover, the boiling-points of mixtures of the two compounds rise evenly from that of the chloride to that of the bromide, whilst the freezing-point curve of such mixtures is a smooth mixed-crystal curve, giving no indication of the existence of any intermediate compound.

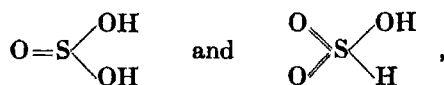
The remaining compounds of bromine and all those of iodine corresponding with thionyl and sulphuryl chlorides and chlorosulphonic acid are either unknown or their existence is very doubtful. There is no reaction between sulphur dioxide and bromine analogous to that by which sulphuryl chloride is formed from sulphur dioxide and chlorine; this is true between 100° and 200° C., both in the dark and under strong illumination, also in the presence of likely catalysts.²

SULPHUR AND OXYGEN.

Judging from the valency of sulphur in its hydrogen compounds one might expect at least one oxygen compound of bivalent sulphur. Such a substance is not known in the free condition although indications of its possible existence have been observed. Attempts to prepare it by heating the sesquioxide, S_2O_3 , *in vacuo* have not been successful.³ The oxygen derivatives of higher valency are more stable and several are known in the free state. An oxy- or hydroxy-derivative of bivalent sulphur occurs only in certain organic compounds of general formula $R.S.OH$. These compounds, which have acidic properties and are termed *sulphenic acids*, are generally unstable. They are derived from the unknown parent substance $H.S.OH$, which may be termed thiohydroperoxide.⁴

Sulphur is probably present in the quadrivalent condition in the organic compounds known as the *sulphorides*, which have the general formula $R-S-R$. The sulphur atom exists in a similar condition in

the alkyl sulphites (the true sulphites), which have the general formula $O=S \begin{smallmatrix} \nearrow OR \\ \searrow OR \end{smallmatrix}$, where R represents an organic radical. The metallic sulphites, however, appear to contain sexavalent sulphur, although sulphurous acid behaves under different conditions as if it possessed two distinct structures, namely,



containing quadrivalent and sexavalent sulphur, respectively.

¹ Mayes and Partington, *loc. cit.*

² Trautz, *Zeitsch. Elektrochem.*, 1915, 21, 329.

³ See Vogel and Partington, *Trans. Chem. Soc.*, 1925, 127, 1514.

⁴ Fries, *Ber.*, 1912, 45, 2965; Zincke, *Annalen*, 1912, 391, 55; Gutmann, *Ber.*, 1908, 41, 1650, 3351; Fromm, *ibid.*, 1908, 41, 3397.

Sexavalent sulphur is the most stable form of combined sulphur. Various hydroxy-derivatives are known. The lowest is the unisolated *sulphoxylic acid*, H_2SO_2 , of which the zinc salt has been obtained by the action of zinc dust on an ether solution of sulphuryl chloride.¹

The structure of this substance appears to be $\begin{array}{c} \text{O} \\ \diagup \text{S} \diagdown \\ \text{O} \quad \text{H} \end{array}$, both from its method of formation and from the ready conversion of its zinc salt into a *sulphone*, which class of organic substance is recognised as containing

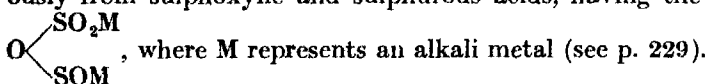
sexavalent sulphur and having the general constitution $\begin{array}{c} \text{O} \\ \diagup \text{S} \diagdown \\ \text{O} \quad \text{R} \end{array}$. It is quite possible that the free substance might also exhibit "tautomerism" (dynamic isomerism) and behave in some reactions according to a structure $\text{H}-\text{S}-\text{OH}$ (of which the *sulphinic acids*, $\text{R}.\text{SO}.\text{OH}$, are



derivatives) or even $\text{HO}.\text{S}.\text{OH}$. The best known derivative of the acid is *sodium formaldehydesulphoxylate* (see p. 228), and this compound on hydrolysis with dilute sulphuric acid yields hydrogen sulphide and sulphurous acid.²

Sodium Sulphoxylate, Na_2SO_2 , may be obtained by the action of sulphur sesquioxide (p. 224) on sodium ethoxide; on the addition of sulphuric acid to the mixture, sodium ethylsulphoxylate, $\text{Na}.\text{C}_2\text{H}_5.\text{SO}_2$, is first formed, which, when kept overnight, undergoes hydrolysis. The solution, acidified with more dilute sulphuric acid, then yields the required sodium salt as a white precipitate which may be separated and dried over phosphorus pentoxide.³ The salt is fairly stable and may be heated to 110°C . without change; on exposure to air, however, it turns yellowish-brown. It is readily soluble in hot water, unattacked by hot mineral acids, but decomposed by a hot mixture of fuming nitric acid and bromine.

The *hydrosulphites*, $\text{M}_2\text{S}_2\text{O}_4$, may be regarded as derived simultaneously from sulphonylic and sulphurous acids, having the constitution



The sulphates and persulphates are all derived from sexavalent sulphur, and the sulphites also appear to belong to the same class, although, as already mentioned (p. 101), the possibility of quadrivalent sulphur is not precluded.

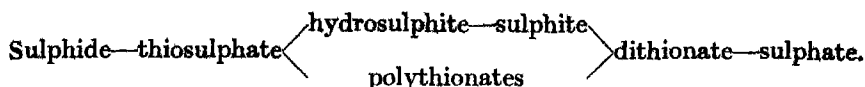
The difference in stability of inorganic substances containing sulphur in varying degrees of valency is reflected in the relative readiness with which they undergo spontaneous oxidation. By treating solutions of such substances with ozonised oxygen, the order in which oxidation occurs has been shown to be :⁴

¹ Fromm and Palma, *Ber.*, 1906, 39, 3317.

² Bassett and Durrant, *J. Chem. Soc.*, 1927, p. 1401. For methods of titrating this compound, see Salkin, *Ind. Eng. Chem.*, 1923, 15, 848.

³ Vogel and Partington, *Trans. Chem. Soc.*, 1925, 127, 1514.

⁴ Riesenfeld and Egidius, *Zeitsch. anorg. Chem.*, 1914, 85, 217.



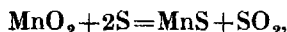
Sulphur Dioxide.

Occurrence.—The gases issuing from volcanoes contain sulphur dioxide in the free condition, and the gas is also present dissolved in the neighbouring springs. Sulphur dioxide is present in minute quantities in the air of towns, especially such as are occupied on an extensive scale with industries consuming much coal. The air of tunnels through which steam locomotives pass is frequently highly charged with sulphur dioxide.

On account of its characteristic odour, sulphur dioxide was early recognised as a product of the combustion of sulphur, although the gas was not isolated until Priestley in 1775, by means of his mercury trough, collected it from the interaction of mercury and sulphuric acid.¹ Lavoisier almost immediately afterwards showed that the new substance was a compound of sulphur and oxygen inferior to sulphuric acid in oxygen content.

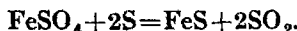
Preparation.—(1) *From Sulphur.*—The simplest method of producing sulphur dioxide consists in burning sulphur in air or oxygen; the element ignites at about 250° to 260° C. The primary product, however, is not perfectly pure dioxide; the product of combustion in oxygen contains 2 or 3 per cent. of sulphur trioxide; ² in air the proportion of trioxide is still higher and may attain to 7 per cent. of the sulphur burnt,³ the nitrogen apparently acting as catalyst. Increase of pressure favours the production of the trioxide,⁴ as its formation involves a greater volume reduction, and experiment shows that under a pressure of 40 to 50 atmospheres of oxygen almost 50 per cent. of the sulphur may be converted into trioxide.

The necessary oxygen need not be obtained from the air. Sulphur dioxide is readily obtained by heating sulphur with certain oxides, dioxides or peroxides. Sulphur vapour and steam heated at a suitable temperature in the presence of iron oxide as catalyst react to form sulphur dioxide and hydrogen which may be recovered separately. With manganese dioxide and powdered sulphur the reaction proceeds as follows :



manganese sulphide constituting the residue.

Similarly, when sulphur is heated with 2 to 3 times its weight of dehydrated ferrous sulphate or copper sulphate, sulphur dioxide is produced together with the sulphide of the metal : ⁵



¹ Priestley, *Experiments on Air*, 1776, ii., 16; 1777, iii., 272; *Experiments and Observations*, 1779, iv., 122.

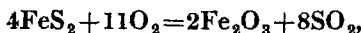
² Lunge and Salathe, *Chem. Zeit.*, 1883, 7, 29; Hempel, *Ber.*, 1890, 23, 1455.

³ Kastle and McHargue, *Amer. Chem. J.*, 1907, 38, 465.

⁴ Giran, *Compt. rend.*, 1904, 139, 1219; 1905, 140, 1704; Cornog, Dargan and Bender, *J. Amer. Chem. Soc.*, 1926, 48, 2757. For the effect of reduced pressure on the oxidation, see Semenov and Rjabinin, *Zeitsch. physikal. Chem.*, 1928, B, 1, 192.

⁵ Stolba, *J. prakt. Chem.*, 1866, 99, 54; Brückner, *Monatsch.*, 1906, 27, 49.

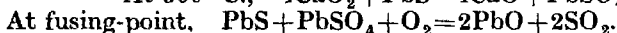
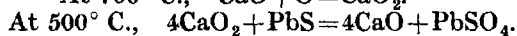
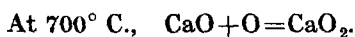
(2) *From Sulphides*.—By heating metallic sulphides in air sulphur dioxide is obtained in a more or less pure condition. In the commercial preparation of sulphuric acid, for example (see p. 150), iron pyrites, FeS_2 , usually containing copper pyrites, $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$, and contaminated with varying amounts of siliceous gangue, arsenic and other compounds, is roasted in air to yield the necessary sulphur dioxide. The main reaction taking place may be represented by the equation :



but in addition to the presence of volatile impurities from the pyrites such as arsenious oxide, sulphur trioxide is also present, for the metallic oxides produced during the roasting process exert a catalytic effect, thereby facilitating the further oxidation of the dioxide.¹

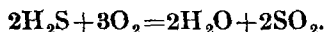
The use of zinc blende and mixed zinc ores as a convenient source of sulphur dioxide for sulphuric acid manufacture has been advocated. The residue from the roasting is often more valuable than in the case of pyrites, but the roasting process is more troublesome and the presence of fluorspar in the blende exerts a deteriorating influence on the lead chambers.²

On roasting lead sulphide (galena) with lime, sulphur dioxide is evolved.³ It is assumed that the reactions which take place are as follows :



Ferrous or manganese oxide may be substituted for lime in the process.⁴

When hydrogen sulphide is burned in excess of air, sulphur dioxide is formed :



This reaction has been made the basis of a patent for the commercial production of the gas.⁵

(3) *From Sulphuric Acid*.—Concentrated sulphuric acid can be made to yield sulphur dioxide by a variety of processes :

(a) If merely raised to a red heat, as, for example, when it is dropped into a red-hot retort, sulphuric acid undergoes decomposition according to the equation :



and the sulphur dioxide can be separated by passing the dried gaseous product through a vessel immersed in a freezing mixture. This method was formerly used in preparing a mixture of sulphur dioxide and oxygen for the manufacture of sulphur trioxide.

(b) Sulphuric acid, when heated with copper or mercury, is reduced to sulphur dioxide. With the former metal, cupric sulphate is formed

¹ Scheurer-Kestner, *Compt. rend.*, 1875, 80, 1230; Lunge and Salathe, *Ber.*, 1877, 10, 1824; Schützenberger, *Bull. Soc. chim.*, 1879, 32, 610.

² Hutin, *Mon. scient.*, 1917, 7, 25.

³ Huntington and Heberlein, *British Patent*, 8064 (1896).

⁴ See also Hardingham, *British Patent*, 3795 (1897); Heyer, *Metall und Erz*, 1925, 22, 439; *Chem. Zentr.*, 1926, i., 464.

⁵ Pernell and Simpson, *British Patent*, 14711 (1886).

together with cuprous sulphide and even cuprous sulphate. The main reaction at a temperature of 130° to 170° C. appears to be :¹

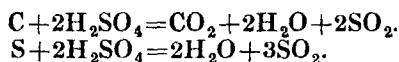


With mercury, the mercuric sulphate may be accompanied by mercurous sulphate.

Under suitable conditions sulphur dioxide may be obtained by the action of sulphuric acid upon many other metals. Thus, finely divided iron decomposes acid of density 1.75 at 200° C., yielding the gas.²

Sulphuric acid is reduced to sulphur dioxide and water by prolonged contact with hydrogen at ordinary temperatures. The reaction is fairly rapid at 250° C.³

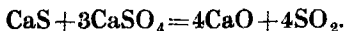
(c) Carbon and sulphur also reduce sulphuric acid, the former giving a mixture containing carbon and sulphur dioxides, whilst the latter yields a steady stream of pure sulphur dioxide. In the laboratory preparation of the gas from sulphuric acid and sulphur, however, it is necessary to have a wide delivery tube to prevent the exit being choked by the sulphur.⁴ The reactions are :



Both of the foregoing methods have been used commercially in preparing sulphur dioxide.⁵

(4) *From Salts.*—(a) Sulphites, thiosulphates and polythionates readily liberate sulphur dioxide when treated with an acid, or, in the case of the salts of the heavier metals, when merely heated. Calcium sulphite mixed with plaster of Paris and moulded into cubes forms a suitable material for use with sulphuric acid in an automatic gas generator such as Kipp's apparatus.⁶

(b) When the sulphates of the metals of the alkaline earths are heated in the presence of a suitable metal such as iron, or the lower oxides of certain metals, or carbon, sulphur dioxide is obtained.⁷ The sulphates are reduced to the corresponding sulphides. The reduction is complete in half an hour at 750° C. for calcium sulphate, at 850° C. for strontium sulphate and at 950° C. for barium sulphate. At temperatures of about 150° C. higher and with an insufficiency of iron, a rapid evolution of sulphur dioxide takes place. The mixture $16\text{CaSO}_4 + 15\text{Fe}$ gives an 80 per cent. theoretical yield of sulphur dioxide. As a result of these reactions certain well-defined ferrites are formed, for example, $\text{Ca}_3\text{Fe}_2\text{O}_8$, $\text{Sr}_2\text{Fe}_2\text{O}_8$ and BaFe_2O_4 .⁸ Gypsum heated at 1400° C. with blast furnace slag containing calcium sulphide gives a high yield of sulphur dioxide :⁹



Several other processes have been devised for utilising *gypsum* and *anhydrite* as sources of sulphur dioxide; for example, the mineral may

¹ Druce, *Chem. News*, 1928, 136, 81.

² Hart, *British Patent*, 13950 (1885).

³ Berthelot, *Compt. rend.*, 1897, 125, 743; Warner, *Chem. News*, 1873, 28, 13.

⁴ Melsens, *Compt. rend.*, 1873, 76, 92.

⁵ See *German Patents*, 196371 (1908) and 22365 (1882), respectively.

⁶ Neumann, *Ber.*, 1887, 20, 1584.

⁷ *British Patent*, 149662 (1921).

⁸ Martin and Fuchs, *Zeitsch. anorg. Chem.*, 1922, 125, 307.

⁹ Neumann, *Zeitsch. angew. Chem.*, 1926, 39, 1537.

be heated at 800° C. with coke, coal, or powdered shale and clay in a slightly oxidising atmosphere, when cement remains as a marketable residue, and the exit gases contain 6 to 7 per cent. of sulphur dioxide.¹

Physical Properties.—Sulphur dioxide is a colourless gas possessing a pungent, choking odour, and exerting an extremely irritating action on the mucous membrane. In consequence of this it has been used in poison gas warfare, but it is not efficient against well-equipped troops on account of the ease with which it is extracted from the air by respirators. Approximately 0.0005 per cent. can be detected by the sense of smell, whilst 0.05 per cent. is unendurable.² Vegetation is injured if the concentration of the gas exceeds 0.003 per cent.

At 15° C. and 760 mm. pressure one litre of sulphur dioxide weighs 2.9266 grams;³ 1000 cub. ft. weigh 172.61 lb., whilst 1 lb. of the gas occupies 5.79 cub. ft. The weight of a litre of sulphur dioxide under varying pressures is as follows:⁴

Pressure in mm. Hg.	Weight of 1 litre of SO ₂ at 0° C. (grams).
760	2.92664
570	2.18172
380	1.44572

The relation between the weight of the gas at a pressure p , namely W_p , and the weight at 760 mm. (W_{760}) is given by the expression:⁵

$$W_{760} = W_p \frac{760}{p} [1 + 323 \times 10^7 (760 - p)].$$

The critical temperature and pressure are, respectively, 157.5° C. and 77.8 atmospheres (see p. 112). At 0° C. the coefficient of expansion is 0.003978, and between 0° and 20° C. 0.00396, a value that is above the value for permanent gases.⁶ At higher temperatures, however, the coefficient becomes smaller, and between 400° and 1700° C. possesses the normal value. Between these two temperatures, therefore, there must be an absence of any appreciable decomposition or dissociation.⁷ The degree of dissociation into sulphur and oxygen at 1500° C. and 1 atmosphere pressure is 5.9×10^{-5} , whilst under a pressure of 0.01 atmosphere⁸ it is 27×10^{-5} .

¹ See also Molitor, *Chem. Zest.*, 1927, 51, 329, 370; Müller, *Zeitsch. angew. Chem.*, 1926, 39, 169.

² See the Selby Smelter Commission, U.S. Bureau of Mines, Bulletin No. 98.

³ Jaquero and Pmtza, *Compt. rend.*, 1904, 139, 129; Baume, *J. Chim. Phys.*, 1908, 6, 1. Leduc (*Compt. rend.*, 1893, 117, 219) gave the value 2.9267. Other data are given by Cailletet and Mathias, *Compt. rend.*, 1887, 104, 1564; Linde, *Ann. Phys. Chem.*, 1895, 56, 563; Bauer, *ibid.*, 1895, 55, 184; Berthelot, *Compt. rend.*, 1898, 126, 1418.

⁴ Jaquero and Pmtza, *loc. cit.*

⁵ Leduc, *loc. cit.*

⁶ Leduc, *Compt. rend.*, 1893, 117, 219; Amagat, *ibid.*, 1869, 68, 1170; 1871, 73, 183; 1872, 74, 1299; Berthelot, *ibid.*, 1898, 126, 1418; Walker, *Proc. Roy. Soc.*, 1903, 72, 24.

⁷ Langer and Meyer, *Ber.*, 1885, 18, 1803.

⁸ Ferguson, *J. Amer. Chem. Soc.*, 1919, 41, 69.

The refractive index for sodium light is 1.00061 at 0° C. and 760 mm.¹ The electrical conductivity is exceedingly small.² The specific heat of sulphur dioxide is 0.1544 (water=1),³ and the ratio $\frac{C_p}{C_v}=1.290$,⁴ a value agreeing quite well with that usual for tri-atomic gases, namely 1.30. Measurement has also been made of the gaseous viscosity, which is 1.253×10^{-4} C.G.S. units at 18.0° C. and 1.630×10^{-4} at 100° C.⁵ Investigation of the dielectric constant for gaseous sulphur dioxide is rendered difficult by the tendency of the gas to decompose under electrical stress. The value at 0° C. and atmospheric pressure has been found to be ⁶ 1.00993. The electric moment of the gas, calculated from Debye's equation,⁷ has the value (in C.G.S. E.S.U. $\times 10^{18}$) of 1.611.

The ultra-violet absorption spectra of the gas and its aqueous solutions have been investigated. In the case of the gas the most distinct absorption band lies between 317.9 and 263.0 $\mu\mu$,⁸ whilst solutions of the gas exhibit a characteristic band at 276 $\mu\mu$.⁹ Absorption of the infra-red by sulphur dioxide has also been studied.¹⁰

Sulphur dioxide is diamagnetic; at 0° C. and 760 mm. pressure the magnetic susceptibility¹¹ is -8.5×10^{-10} .

The gas is readily soluble in water, the process of solution being accompanied by an evolution of heat. The heats of solution for various concentrations have been measured¹² at 25° C., and the relation between $-\Delta H$, the total heat of solution per gram-molecule of SO₂ dissolved, and N , the number of molecules of water to one molecule of SO₂, is found to be

$$-\Delta H = 4911.6 + 1105.26 \log N.$$

The following table gives typical experimental data :

¹ Blockrode, *Proc. Roy. Soc.*, 1884, 37, 339; Walker, *ibid.*, 1903, 72, 24; Cuthbertson and Parr, *ibid.*, 1908, [A], 80, 406; Cuthbertson, *ibid.*, 1910, [A], 83, 171.

² Bartoli, *Gazzetta*, 1895, 25, 1, 205.

³ Regnault, *Jahresber.*, 1863, p. 84.

⁴ Partington and Cant, *Phil. Mag.*, 1922, [vi.], 43, 369.

⁵ Smith, *ibid.*, 1922, [vi.], 44, 508; Meyer, *Ann. Phys. Chem.*, 1871, [ii.], 143, 14; 1873, 148, 526; Trautz and Weizel, *Ann. Physik*, 1925, iv., 78, 305.

⁶ Klemencič, *Rep. d. Phys.*, 1885, 21, 571; *Wien Akad. Ber.*, 1885, 91, 2, 712; Baedeker, *Zeitsch. physikal. Chem.*, 1901, 36, 305.

⁷ Zahn, *Phys. Review*, 1926, ii., 27, 455.

⁸ Liveing and Dewar, *Chem. News*, 1883, 47, 121.

⁹ Baly and Bailey, *Trans. Chem. Soc.*, 1922, 121, 1813. See also Wright, *ibid.*, 1914, 105, 673; Garrett, *ibid.*, 1915, 107, 1324; Baly and Garrett, *Phil. Mag.*, 1916, [vi.], 31, 512; Garrett, *ibid.*, p. 505; Getman, *J. Physical Chem.*, 1926, 30, 266.

¹⁰ Bahr, *Ann. Physik*, 1910, [4], 33, 585; Rubens and von Wartenberg, *Physikal. Zeitsch.*, 1911, 12, 1080.

¹¹ Pascal, *Compt. rend.*, 1909, 148, 413; *Ann. Chim. Phys.*, 1910, [8], 19, 1.

¹² Stiles and Felsing, *J. Amer. Chem. Soc.*, 1926, 48, 1543. See also Thomsen, *Ber.*, 1873, 4, 713; Favre, *Ann. Chem. Phys.*, 1874, [v.], 1, 247; Berthelot, *Compt. rend.*, 1883, 96, 142.

TOTAL HEAT OF SOLUTION OF SULPHUR DIOXIDE.

Δt , °C.	Grams SO_2 .	Grams H_2O .	$\frac{\text{Mols. H}_2\text{O}}{\text{Mols. SO}_2}$	$-\Delta H$ Obs., cal./mol.	$-\Delta H$, Calculated from Equation, cal./mol.
0.180	0.2712	168.28	2140.9	8587	8592
0.260	0.8936	160.12	1446.6	8412	8405
0.447	0.7448	172.59	824.01	8122	8134
0.658	1.0973	168.18	545.01	7946	7936
0.947	1.6411	170.83	370.15	7745	7550
1.768	3.1480	167.59	189.30	7421	7428
4.190	7.9602	168.76	75.29	6994	6986

Below 50° C. the solubility of sulphur dioxide in water does not obey Henry's Law. In the following table the solubility is given as grams of sulphur dioxide per 100 grams of water when the partial pressure of the gas is equal to 760 mm. of mercury.

SOLUBILITY OF SULPHUR DIOXIDE IN WATER.

Temperature, °C.	Grams SO_2 per 100 grams H_2O .		Temperature, °C.	Grams SO_2 per 100 grams H_2O .	
	(a). ¹	(b). ¹		(a). ¹	(b). ¹
10	15.4	15.39	30	7.8	7.56
15	12.55	12.73	40	5.8	5.54
20	10.4	10.64	50	4.5	4.14
25	8.95	8.98	60	..	3.24

At 15° C. and 760 mm., 1 c.c. of water absorbs approximately 44 c.c. of the gas.

The density of the saturated solution is as follows : at 0° C., 1.061 ; at 10° C., 1.055 ; at 20° C., 1.024. The following determinations for solutions of various concentrations have been made at 15.5° C. : ²

SO_2 (per cent.)	0.99	2.05	2.87	4.04	4.99	5.89
$D_4^{15.5}$	1.0041	1.0092	1.0138	1.0194	1.0242	1.0287

SO_2 (per cent.)	7.01	8.08	8.68	9.80	10.75
$D_4^{15.5}$	1.0343	1.0389	1.0428	1.0482	1.0530.

¹ (a) Sims, *Trans. Chem. Soc.*, 1862, 14, 1 ; (b) Hudson, *ibid.*, 1925, 127, 1332. See also Schönfeld, *Annalen*, 1855, 95, 1 ; Carius, *ibid.*, 94, 148 ; Wiedemann, *Ann. Phys. Chem.*, 1882, 17, 349 ; van der Waals, *Ber.*, 1885, 28, 599 ; Lindner, *Ber. K. Akad. Wiss. Wien*, 1912, 121, 293 ; Froese, *Chem. Zeitsch.*, 1920, 44, 294 ; Smith and Parkhurst, *J. Amer. Chem. Soc.*, 1922, 44, 1918 ; Sherwood, *Ind. Eng. Chem.*, 1925, 17, [7], 745.

² Giles and Shearer, *J. Soc. Chem. Ind.*, 1885, 4, 303.

The aqueous solutions decompose slowly at ordinary temperatures, depositing sulphur, sulphuric acid being formed in solution. At 160°C . the decomposition is rapid.¹

Under suitable conditions solid products of variable composition may be obtained from aqueous solutions of sulphur dioxide, and hydrates containing 6 to 15 molecules of water have been described.² It has been shown by a more recent investigation,³ however, that only one hydrate, namely $\text{SO}_2 \cdot 6\text{H}_2\text{O}$, is formed. This gives a eutectic with ice at -2.6°C . The so-called higher hydrates consist of mixtures of the hexahydrate with ice.

Certain organic liquids also dissolve sulphur dioxide, and a direct comparison of the solubility in water and in chloroform has been effected by "partition" experiments,⁴ in which measurement is made of the distribution of the gas between the two solvents in contact with one another.

Alcohol is superior to water as a solvent for sulphur dioxide, absorbing more than 200 times its own volume of the gas at 0°C . and 760 mm.;⁵ thus, 1 c.c. of alcohol absorbs the following volumes :

Temperature, $^{\circ}\text{C}$.	Volume of Gas dissolved, c.c.	Temperature, $^{\circ}\text{C}$.	Volume of Gas dissolved, c.c.
0	216	15	116
5	175	20	96
10	142	25	84

Acetic acid⁶ under similar conditions dissolves more than 300 volumes or almost its own weight of the gas. Acetone⁷ dissolves about twice its weight or nearly 600 times its volume of sulphur dioxide, whilst camphor⁸ also absorbs more than 300 times its volume, forming a liquid solution. In the last two cases chemical combination undoubtedly occurs; the freezing-point curve of camphor-sulphur dioxide mixtures indicates the formation of two unstable compounds, namely, $\text{C}_{10}\text{H}_{16}\text{O} \cdot 2\text{SO}_2$, m.pt. -45°C ., and $\text{C}_{10}\text{H}_{16}\text{O} \cdot \text{SO}_2$, m.pt. -24°C .; these are probably active in the preparation of sulphuryl chloride in the presence of camphor. The use of methylcyclohexanone has been recommended

¹ Jungfleisch and Brunel, *Compt. rend.*, 1913, 156, 1719.

² E.g. $\text{SO}_2 \cdot 6\text{H}_2\text{O}$, Villard, *Ann. Chim. Phys.*, 1897, [7], 11, 289; $\text{SO}_2 \cdot 7\text{H}_2\text{O}$, Geuther, *Annalen*, 1884, 224, 218; $\text{SO}_2 \cdot 9\text{H}_2\text{O}$, Pierre, *Ann. Chim. Phys.*, 1848, [3], 23, 416; $\text{SO}_2 \cdot 11\text{H}_2\text{O}$, Döpping, *Petersb. Akad. Bull.*, 1847, 7, 100; $\text{SO}_2 \cdot 15\text{H}_2\text{O}$, de la Rive, *Ann. Chim. Phys.*, 1828, [2], 40, 405.

³ Tammann and Krige, *Zeitsch. anorg. Chem.*, 1925, 146, 179. See also Roozeboom, *Zeitsch. physikal. Chem.*, 1888, 2, 440.

⁴ McCrae and Wilson, *Zeitsch. anorg. Chem.*, 1903, 35, 11; Drucker, *Zeitsch. physikal. Chem.*, 1904, 49, 579.

⁵ Carius, *loc. cit.* See also Endemann, *Annalen*, 1866, 140, 336; Paghani, *Ber.*, 1878, 11, 155; Berthelot, *Ann. Chim. Phys.*, 1898, [vii.], 14, 289.

⁶ Schulze, *J. prakt. Chem.*, 1881, [ii.], 24, 168; Cupr, *Pub. Fac. Sci. Univ. Masaryk*, 1926, No. 68.

⁷ Schulze, *loc. cit.* For the solubility of liquid sulphur dioxide in *n*-hexane, see Seyer and Gill, *Trans. Roy. Soc. Canada*, 1924, iii., 18, III., 209; in cetene, see Seyer and Hugget, *ibid.*, p. 213.

⁸ Bellucci and Grassi, *Atti R. Accad. Lincei*, 1913, [5], 22, ii., 676; Schulze, *loc. cit.*, p. 172; Bineau, *Ann. Chim. Phys.*, [iii.], 34, 326.

as an absorbing liquid for the recovery of sulphur dioxide from waste gases.¹

Sulphur dioxide dissolves in aqueous solutions of inorganic salts frequently more readily than in pure water. With most salts, excluding sulphates, compounds appear to be formed in solution of the general type $\text{MX} \cdot \text{SO}_2$, where M and X stand for univalent metal and negative radical, respectively.² The solubility curve of sulphur dioxide in sulphuric acid of concentration ranging from 55 to 98.5 per cent. is interesting. A minimum occurs at 85.8 per cent. acid, and from that point the curve inclines sharply upwards for both increase or decrease of sulphuric acid concentration.³

SOLUBILITY OF SULPHUR DIOXIDE IN SULPHURIC ACID AT 20° C. AND 760 MM.⁴

Sulphuric Acid, per cent.	Grams SO_2 in 100 grams of Acid.	Sulphuric Acid, per cent.	Grams SO_2 in 100 grams of Acid.
55.1	5.13	86.5	2.82
68.9	4.16	88.1	2.90
80.2	3.12	90.8	3.10
82.5	2.99	92.8	3.21
84.2	2.88	94.6	3.50
85.8	2.83	96.5	3.83
85.8	2.80	98.5	4.03

At the point of minimum solubility of the sulphur dioxide the composition of the solvent closely approximates to that required for the monohydrate $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (namely 84.5 per cent. acid), and it is significant that other physical properties of the acid pass through critical values at this concentration (see p. 168).

Sulphuryl chloride, SO_2Cl_2 , is a still better solvent for sulphur dioxide and can absorb 187 volumes of the gas at the ordinary temperature.

Wood charcoal at 0° C. readily absorbs gaseous sulphur dioxide up to a volume even exceeding 100 times that of the charcoal; ⁵ platinum black absorbs the gas to a relatively slight extent.⁶ The gas is also absorbed very appreciably by caoutchouc, the process merely being one of solution.⁷ The adsorption of sulphur dioxide by silicic acid

¹ Weissenberger and Piatti, *Chem. Zeit.*, 1929, 53, 245, 266.

² Fox, *Zeitsch. physikal. Chem.*, 1902, 41, 458. See also Hudson, *Trans. Chem. Soc.*, 1925, 127, 1332.

³ Miles and Fenton, *Trans. Chem. Soc.*, 1920, 117, 59; cf. Cupr, *Pub. Fac. Sci. Univ. Masaryk*, 1926, No. 68.

⁴ For the solubilities of sulphur dioxide in sulphuric acid of varying density and at various temperatures, see Kolb, *Bull. Soc. Ind. Mulhouse*, 1872, p. 222; *Dingl. poly. J.*, 1873, 209, 268; Dunn, *Chem. News*, 1882, 45, 270. For the solubility of sulphur dioxide in suspensions of calcium and magnesium hydroxides, see Smith and Parkhurst, *J. Amer. Chem. Soc.*, 1922, 44, 1918; Riou and Bérard, *Compt. rend.*, 1928, 186, 1433.

⁵ Favre, *Ann. Chim. phys.*, 1874, [v.], 1, 244; Kayser, *Ann. Phys. Chem.*, 1881, [iii.], 12, 526; Henglein and Grzenkovski, *Zeitsch. angew. Chem.*, 1925, 38, 1186; Póányi and Welke, *Zeitsch. physikal. Chem.*, 1928, 132, 371.

⁶ Chappuis, *Ann. Phys. Chem.*, 1883, [iii.], 19, 21.

⁷ Reychler, *Bull. Soc. chim.*, 1893, [iii.], 9, 404; *J. Chim. phys.*, 1910, 8, 3617.

gels has been measured. It is found that the maximum adsorption is exhibited by gels containing about 7 per cent. of water. In the absence of air the adsorption is reversible.¹ Glass also adsorbs sulphur dioxide to a marked degree, depending on the time of contact,² and it has been found impossible to remove the adsorbed gas completely from glass wool.³

The formation of sulphur dioxide from rhombic sulphur and gaseous oxygen is exothermic to the extent of 71.08 Cals., the value being slightly higher, namely 71.72 Cals., for formation from monoclinic sulphur, the difference being due to the heat of transformation of a gram-atomic weight of sulphur from the rhombic to the monoclinic form.

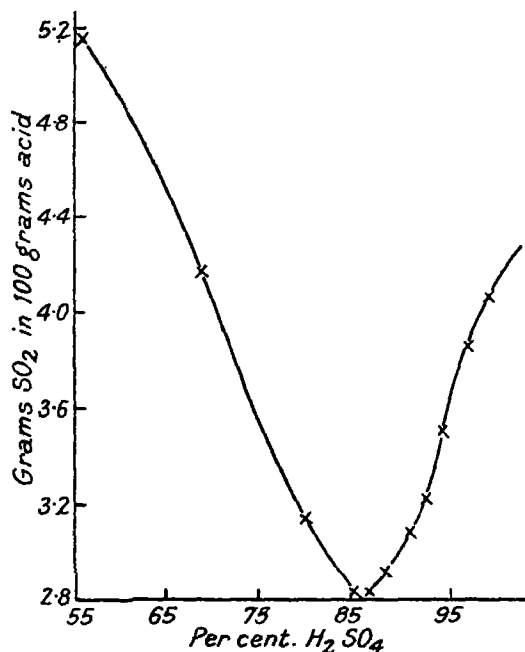


FIG. 8. —Solubility of Sulphur Dioxide in Sulphuric Acid at 20° C.

Liquid Sulphur Dioxide.—Sulphur dioxide was the first gas to be converted to the liquid state.⁴ It can be liquefied by passage through a tube cooled to below $-10^{\circ}C$. in a freezing mixture,⁵ but commercially the liquid is produced by compression.⁶ The sulphurous gases from burning iron pyrites or some other suitable source, containing some

¹ McGavack and Patrick, *J. Amer. Chem. Soc.*, 1920, 42, 946; cf. Fical, *Giorn. Chim. Ind. Appl.*, 1928, 10, 199. Measurements of the heat of adsorption have been made by Patrick and Greider, *J. Physical Chem.*, 1925, 29, 1031. For adsorption by titania gel, see Klosky and Burggraft, *J. Amer. Chem. Soc.*, 1928, 50, 1045.

² Crespi and Moles, *Anal. Fis. Quim.*, 1926, 24, 452.

³ Bangham and Burt, *J. Physical Chem.*, 1925, 29, 540.

⁴ See Fourcroy, *Systèmes des connaissances chimiques*, 1800, vol. u., p. 74.

⁵ Loir and Drion, *Bull. Soc. chim.*, 1860, 2, 185.

⁶ Hänisch and Schröder, *Zeitsch. angew. Chem.*, 1888, 1, 448; Lange, *ibid.*, 1890, 12, 275, 300; Harpf, *Arens Sammlung*, 1900, p. 235. See also Melsens, *Phil. Mag.*, 1873, [iv.], 46, 410. German Patents, 36721 (1886); 52025 (1890).

6 per cent. of sulphur dioxide, or certainly not less than 4 per cent., are extracted by cold water trickling down a tower and meeting the ascending gases; the solution thus obtained contains about 1 per cent. of the dioxide, and on warming, the dissolved dioxide is expelled. After being dried by passage through cooled pipes and finally through a chemical dehydrating agent such as sulphuric acid, the gas is liquefied by compression and the liquid enclosed in steel cylinders or, for smaller quantities, in glass cylinders. The liquid finds use in some ice-producing machines and also provides a convenient means of storing the substance.

Liquid sulphur dioxide is a colourless mobile fluid which boils at $-10.02 \pm 0.1^\circ \text{C.}$ at 760 mm.;¹ the density varies considerably with the temperature,² as indicated in the following table:

Temperature, °C.	Density.	Coefficient of Expansion.	Temperature, °C.	Density.	Coefficient of Expansion.
-40	1.5331	0.00157	40	1.3264	0.00223
-20	1.4846	0.00164	60	1.2633	0.00261
0	1.4350	0.00175	80	1.1920	0.00315
2	1.3831	0.00192	100	1.1100	0.00390

The latent heat of evaporation per gram-molecule is 6150 calories,³ whilst the specific heat between -20° and $+10^\circ \text{C.}$ is approximately 0.318.⁴ The vapour pressures at various temperatures from -20° to $+30^\circ \text{C.}$ are given in the following table:

Temperature, °C.	-20	-10	0	+10	+20	+30
Vapour pressure (atm.) .	0.65	1.04	1.58	2.34	3.35	4.67

The vapour pressure⁵ of sulphur dioxide at 50°C. is only about 8 atmospheres, although at 110°C. it exceeds 30 atmospheres, so that the sealed containing vessels are not likely to be submitted to very great strain so long as care is taken to prevent heating. The critical temperature is $157.50 \pm 0.05^\circ \text{C.}$ and the critical pressure 77.79 ± 0.05 atmospheres.⁶

¹ Gibbs, *J. Amer. Chem. Soc.*, 1905, 27, 851; Bergstrom, *J. Physical Chem.*, 1922, 26, 876.

² Cailletet and Mathias, *Compt. rend.*, 1887, 104, 1563; Bleekrode, *Proc. Roy. Soc.*, 1885, 37, 339; Lange, *Zeitsch. angew. Chem.*, 1899, 12, 277; Nasini, *Ber.*, 1882, 15, 2884; Previe, *Ann. Chim. Phys.*, 1847, [iii.], 21, 342; Drion, *ibid.*, 1854, [in.], 41, 36; Andréef, *Annalen*, 1859, 110, 1.

³ Mathias, *Compt. rend.*, 1888, 106, 1148; 1894, 119, 851; Vaubel, *J. prakt. Chem.*, 1898, [ii.], 57, 35; Burrell and Robertson, *J. Amer. Chem. Soc.*, 1915, 37, 2691; Thomsen, *Thermochemistry* (translated by Burke), 1908 (Longmans & Co.).

⁴ Mathias, *loc. cit.*

⁵ Cardoso and Fiorentino, *J. Chim. phys.*, 1926, 23, 841; Cardoso, Coppola and Fiorentino, *Chem. Zentr.*, 1924, 1, 1975; Stock, Henning and Kuss, *Ber.*, 1921, 54, [B], 1119; Mund, *Bull. Acad. roy. Belg.*, 1919, [v.], 5, 529; Burrell and Robertson, *loc. cit.*; Briner and Cardoso, *Compt. rend.*, 1907, 144, 911; Regnault, *ibid.*, 1860, 50, 1063. See also Maass and Maass, *J. Amer. Chem. Soc.*, 1928, 50, 1352.

⁶ Cardoso and Fiorentino, *loc. cit.*; Cailletet and Mathias, *loc. cit.*; Centnerszwer, *J. Russ. Phys. Chem. Soc.*, 1903, 35, 742; Guze, *Arch. Sci. phys. nat.*, 1890, [iii.], 23, 204.

The critical density is 0.5240 ± 0.0005 .¹ Measurement has also been made of the viscosity,² the refractive index ($n_D^{18} = 1.350$)³ and the compressibility.⁴

The surface tensions of the liquid have been determined by the capillary tube method, and between -20°C. and 50°C. the values agree to within 5 per cent. with the equation :

$$\gamma(\text{dynes/cm.}) = 0.061534(157.5 - t)^{1.2},$$

and there appears to be no evidence of association of molecules over this range of temperature.⁵

Although liquid sulphur dioxide is practically a non-conductor of electricity (its specific conductivity is 0.85×10^{-7} at 15°C.), it dissolves many substances giving solutions which conduct the electric current.⁶ Some salts, indeed, conduct better in liquid sulphur dioxide solution than in aqueous solution. The halides of the alkali metals, including ammonium and the alkylammoniums such as $\text{N}(\text{CH}_3)_4\text{Cl}$, produce solutions which, during electrolysis, yield the halogen at the anode, whilst sulphur is deposited on the cathode and a sulphite simultaneously formed. Cady and Taft, however, could detect no free sulphur in the cathode deposits obtained by electrolysis of solutions containing potassium iodide, iodate, ferriyanide or similar salt. In some cases the formation of additive compounds between solvent and solute has been detected, e.g. $\text{KI} \cdot 4\text{SO}_2$, m.pt. $+0.26^\circ \text{C.}$; KISO_2 , m.pt. -23.4°C. It has been suggested that the ionising power of sulphur dioxide may be connected with its high dielectric constant, 14.8 at 23°C.

Many organic substances⁷ are soluble in liquid sulphur dioxide, e.g. many alcohols, ether, resins, carbon disulphide, chloroform, benzene and alkaloids.⁸ It has been shown that under ordinary working conditions di-olefines are soluble and mono-olefines insoluble in liquid sulphur dioxide. This difference in solubility may be advantageously utilised in the refining of mineral lubricating oils, but it does not appear possible to separate naphthenes from paraffins by this method.⁹

Phosphorus and sulphur are only sparingly soluble in the liquid, but sulphur monochloride is miscible.¹⁰ The binary systems formed by liquid sulphur dioxide with the tetrachlorides of carbon, tin and titanium, and with the tetrabromide of tin, have been investigated. The liquids are only partly miscible at lower temperatures and compound

¹ Cardoso and Sorrentino, *J. Chim. phys.*, 1927, 24, 65, 77.

² Fitzgerald, *J. Physical Chem.*, 1912, 16, 621.

³ Bleekrode, *Proc. Roy. Soc.*, 1884, 37, 339; *Rec. Trav. chim.*, 1886, 4, 77.

⁴ Cailliet, *Compt. rend.*, 1872, 75, 77.

⁵ Stowe, *J. Amer. Chem. Soc.*, 1929, 51, 410. See also Clarke, *Chem. News*, 1878, 38, 294; Hannay, *Proc. Roy. Soc.*, 1880, 30, 478.

⁶ Walden, *Ber.*, 1899, 32, 2862; Walden and Centnerszwer, *Bull. Acad. Sci. St. Petersburg*, 1902, 15, [v.], 17; *Zeitsch. physikal. Chem.*, 1903, 42, 432; Bagster and Steele, *Trans. Faraday Soc.*, 1912, 8, 51; *Chem. News*, 1912, 105, 157, 169; Franklin, *J. Physical Chem.*, 1911, 15, 675; Dutoit and Gyr, *J. Chim. phys.*, 1909, 7, 189; Carvallo, *Compt. rend.*, 1910, 151, 717; 1913, 156, 1882, Centnerszwer and Drucker, *Zeitsch. Elektrochem.*, 1923, 29, 210; Cady and Taft, *J. Physical Chem.*, 1925, 29, 1075.

⁷ Sestini, *Bull. Soc. chim.*, 1868, 10, [ii.], 226; de Carli, *Gazzetta*, 1927, 57, 347.

⁸ Shorry, *J. Physical Chem.*, 1907, 11, 559; Mund and Herrent, *J. Chim. phys.*, 1924, 21, 51.

⁹ Seyer and Huggett, *Trans. Roy. Soc. Canada*, 1924, [iii.], 18, III., 213; Seyer and Gill, *ibid.*, p. 209; Seyer and Gallagher, *ibid.*, 1926 [iii.], 20, III., 343.

¹⁰ Prinz, *Annalen*, 1884, 223, 355.

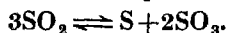
formation does not occur. With carbon tetrachloride, the critical solution temperature is -29.3°C. , two liquid phases being possible down to -45°C. ¹

The molecular ebullioscopic constant of sulphur dioxide is 15.0.

When free from moisture, liquid sulphur dioxide is without action on iron and metals generally.² The commercial liquid is generally quite free from sulphur trioxide.³

Solid Sulphur Dioxide has been obtained by rapid evaporation of the liquid, part of which becomes cooled to the point of solidification. The solid is colourless and melts at -72.7°C. ⁴

Chemical Properties.—Gaseous sulphur dioxide exhibits a tendency to undergo chemical change with formation of an equilibrium mixture with sulphur trioxide and sulphur :



Thus it becomes cloudy when exposed to strong illumination,⁵ and the presence of free sulphur in the gas at 1200°C. can be detected by Deville's "hot and cold tube" method.⁶ Light of any wave-length, within the absorption band (see p. 107), if it is of sufficient intensity, is capable of bringing about the decomposition of sulphur dioxide.⁷ The change does not take place, however, if the gas is absolutely dry.⁸ Slow decomposition as represented by the foregoing equation can also be effected by subjecting the gas to prolonged spark discharge.⁹ In all probability this conversion of sulphur dioxide into sulphur and sulphur trioxide is merely a special example of the power of gaseous sulphur dioxide at high temperatures to effect the oxidation of reducing agents such as hydrogen and carbon, the reducing agent or oxidisable substance in this case being part of the sulphur dioxide itself. At 2200°Abs. sulphur dioxide is not appreciably dissociated.¹⁰

In the dry condition both gaseous and liquid sulphur dioxide are without action on dry litmus paper. Dry sulphur dioxide does not react with dry hydrogen at 100°C. or 280°C. ¹¹

Sulphur Dioxide as an Oxidising Agent.—Sulphur dioxide does not support the combustion of most substances which burn in oxygen, but many metals, *e.g.* sodium, potassium, magnesium and finely divided lead, when heated in a stream of the gas undergo conversion into a mixture of sulphide and oxide or sulphite, so much heat being liberated that the mass becomes incandescent; in the case of the alkali metals some thiosulphate also may be formed.¹²

¹ Bond and Beach, *J. Amer. Chem. Soc.*, 1926, 48, 348.

² Lange, *Zeitsch. angew. Chem.*, 1899, 12, 300.

³ Eckman, *Sci. Papers U.S. Bureau Stand.*, No. 554, 1927, 22, 277.

⁴ Mitchell, *Annalen*, 1841, 37, 356; Faraday, *Compt. rend.*, 1861, 53, 846; Walden and Centnerszwer, *loc. cit.*

⁵ Morren, *Compt. rend.*, 1869, 69, 397; Berthelot and Gaudechon, *ibid.*, 1910, 150, 1517.

⁶ Deville, *Bull. Soc. chim.*, 1865, [ii.], 3, 366; Walden and Centnerszwer, *loc. cit.*

⁷ Hill, *Trans. Faraday Soc.*, 1924, 20, 107.

⁸ Coehn and Becker, *Zeitsch. physikal. Chem.*, 1910, 70, 89.

⁹ Buff and Hofmann, *Annalen*, 1860, 113, 129; Berthelot, *Compt. rend.*, 1883, 96, 298.

¹⁰ von Wartenberg, *Zeitsch. anorg. Chem.*, 1908, 56, 320; Ferguson, *J. Amer. Chem. Soc.*, 1919, 41, 69.

¹¹ Berthelot, *Compt. rend.*, 1897, 125, 743.

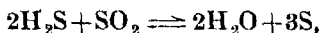
¹² Schiff, *Annalen*, 1861, 117, 92; Guntz, *Bull. Soc. chim.*, 1892, [iii.], 7, 275; Buff and Hofmann, *loc. cit.*

Molten copper absorbs several times its volume of sulphur dioxide, the product being a mixture of cuprous oxide and cuprous sulphide, which remains in solution in the metal.¹ When dry, sulphur dioxide has no action on iron even at 100° C., but the metal is slightly attacked by the moist gas.²

Hydrogen may be oxidised by sulphur dioxide under suitable conditions; thus when a mixture of the gases is passed over finely divided nickel or over nickel sulphide at a dull red heat, water, hydrogen sulphide and sulphur are produced.³ If the gases are passed sufficiently slowly the whole of the sulphur dioxide is decomposed. Cobalt sulphide and, with less efficiency, ferrous sulphide, may also be used as catalysts in this hydrogenation.⁴ A similar reaction occurs at a slightly higher temperature in the absence of a catalyst, but in this case the sulphur is obtained mainly in the free condition; the presence of a little water vapour facilitates the reaction.⁵

Hydrogen iodide reduces dry sulphur dioxide to sulphur, but in the presence of moisture, the iodine thus produced tends to oxidise some of the remaining sulphur dioxide to sulphuric acid.⁶

The interaction of hydrogen sulphide and sulphur dioxide to form water and sulphur, according to the equation



does not take place in the absence of a liquid. Liquid hydrogen sulphide and liquid sulphur dioxide do not react even on boiling together. In the ordinary way the presence of a little water enables the interaction to take place, but many liquids other than water, for example, ethyl and methyl alcohols, glycerol and acetone, are able to bring about the reaction. There is no reaction between the gases at the ordinary temperature in the presence of phosphorus oxychloride, chlorobenzene, carbon tetrachloride, benzene, etc. There seems to be no connection between the dielectric constant and the catalytic activity. Sulphur dioxide and hydrogen sulphide do not react in the presence of the vapour of water or alcohol; it is essential that a liquid be present, probably because the liquid acts as a solvent for the gases. Alcohol is more effective than water, the gases being more soluble in alcohol.⁷

At 100° C. there is no appreciable action between the moist gases, but sulphur is deposited on cooling. The reaction at higher temperatures has been investigated by passing the gases in equivalent proportions through a reaction vessel and analysing the rapidly cooled emergent gases. At 300° C. equilibrium is attained very slowly, the reaction taking place on the walls of the vessel. Using quartz powder as a surface catalyst the equilibrium is reached more rapidly, at 450° C.,

¹ Heyn and Bauer, *Metallurgie*, 1906, 3, 82; Schenck and Hempelmann, *Metall und Erz*, 1913, 1, 283; Stubbs, *Trans. Chem. Soc.*, 1913, 103, 1445; Sieverts and others, *Zeitsch. physikal. Chem.*, 1910, 74, 277; 1913, 82, 257.

² See Lange, *Zeitsch. angew. Chem.*, 1899, 12, 275, 303, 595.

³ Neogi and Adhicary, *Zeitsch. anorg. Chem.*, 1910, 69, 209.

⁴ Tomkinson, *Compt. rend.*, 1923, 176, 35.

⁵ Berthelot, *Ann. Chim. Phys.*, 1898, [vii.], 14, 289; Traube, *Ber.*, 1885, 18, 1894.

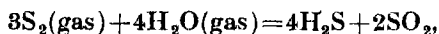
⁶ Mencke, *Chem. News*, 1879, 39, 19; Berg, *Bull. Soc. chim.*, 1900, [iii.], 23, 499; Volhard, *Annalen*, 1887, 242, 93; *Ber.*, 1887, 20, 802.

⁷ Schmid, *Zeitsch. Chem.*, 1868, 11, 50; Hofmann, *Bull. Soc. chim.*, 1876, 26, 324; Klein, *J. Physical Chem.*, 1910, 15, 1; Baker, *Mem. Manchester Phil. Soc.*, 1909, 53, pt. 3; Matthews, *Trans. Chem. Soc.*, 1926, 129, 2270.

while above 600° C. such a catalyst is no longer necessary. The values for the equilibrium constant are given by :

$$K = \frac{[\text{H}_2\text{S}]^4[\text{SO}_2]^2}{[\text{H}_2\text{O}]^4[\text{S}_2]^3},$$

ranging from 1.18 to 0.0062 between 450° and 600° C., and the heat of the reaction,



is of the order of 82.0 klm.-calories, whilst the value calculated from the reaction isochore is 28.0 klm.-calories.¹ The reaction between the mixed gases is also catalysed by active charcoal at lower temperatures, but above 600° C. some sulphur dioxide is reduced by the carbon, whilst above 800° C. carbon disulphide begins to form.

When sulphur dioxide alone is passed over carbon at a red heat the latter undergoes partial oxidation, the products being carbon monoxide, carbon oxysulphide and carbon disulphide; no oxysulphide is obtained at a white heat.² Both carbon monoxide³ and methane are oxidised by sulphur dioxide at high temperatures with formation of sulphur. It has been suggested that volcanic sulphur may, in part, be formed by the reduction of sulphur dioxide by methane, carbon monoxide and hydrogen, all of which are emitted by volcanoes.⁴

Other chemical processes in which sulphur dioxide functions as an oxidising agent include the interaction of sulphur dioxide with stannous chloride or titanous chloride in aqueous solution containing hydrochloric acid, when the salts are converted into the corresponding tetrachlorides;⁵ also the interaction of the gas with organo-magnesium compounds, when the organic sulphide is produced to some extent.⁶

That sulphur dioxide can function either as an oxidising agent or as a reducing agent, according to the conditions, has been shown in the case of certain chlorides, sulphates and phosphates.⁷ The concentration of acid which is added is an important factor, for, by varying the amount present, the sulphur dioxide can be made either to oxidise or to reduce. The action of sulphur dioxide on the chlorides of mercury illustrates this diversity of action. Quantitative results are produced only under very specific conditions. A solution of mercuric chloride (1:80) saturated with sulphur dioxide at 70° to 80° C. and kept at

¹ Grünert, *J. prakt. Chem.*, 1929, [ii.], 122, 1; Randall and von Bichowsky, *J. Amer. Chem. Soc.*, 1918, 40, 356. These values for *K* do not agree with those of Lewis and Randall (*ibid.*, p. 362) at 450° C., probably owing to the latter investigators not recognising the dependence of the equilibria in sulphur vapour on the total pressure. The reaction has also been studied by Lang and Carson, *Proc. Chem. Soc.*, 1905, p. 158; Noack, *Dissertation* (Dresden), 1925; Taylor and Wesley, *J. Physical Chem.*, 1927, 31, 216.

² Berthelot, *Compt. rend.*, 1883, 96, 298; Scheurer-Kestner, *ibid.*, 1892, 114, 296; Smith and Hart, *J. Soc. Chem. Ind.*, 1886, 5, 643; Hänisch and Schroder, *Dingl. poly. J.*, 1885, 258, 225; Fischer and Pranschke, *Brennstoff-Chem.*, 1928, 9, 361.

³ The reaction has been studied by Ferguson, *J. Amer. Chem. Soc.*, 1918, 40, 1626.

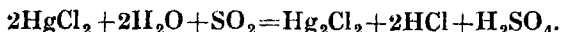
⁴ Papish, *Proc. Indiana Acad. Sci.*, 1918, p. 170.

⁵ Smythe and Wardlaw, *Proc. Durham Phil. Soc.*, 1913-14, 5, 187; *J. Soc. Chem. Ind.*, 1915, 34, 797; Durrant, *Trans. Chem. Soc.*, 1915, 107, 622.

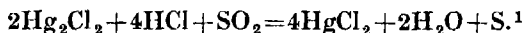
⁶ Oddo, *Gazzetta*, 1911, 41, i., 11.

⁷ Wardlaw and Clews, *Trans. Chem. Soc.*, 1920, 117, 1093; Wardlaw, Carter and Clews, *ibid.*, 1920, 117, 1241; Wardlaw and Pinkard, *ibid.*, 1922, 121, 210; Wardlaw, *J. Soc. Chem. Ind.*, 1926, 45, 210.

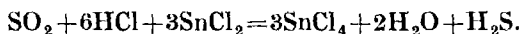
that temperature for a considerable period reacts in accordance with the equation :



In concentrated hydrochloric acid solution sulphur dioxide slowly oxidises mercurous chloride thus :

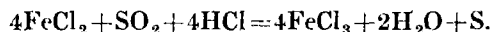


In the case of tin salts the action of sulphur dioxide is complex. In warm acid solution stannous sulphide is first precipitated and then yellow stannic sulphide mixed with sulphur. In highly concentrated acid solution, however, the sulphides are not precipitated, but hydrogen sulphide is evolved :



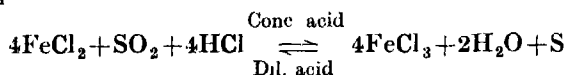
In moderately acid solution the two tin salts and the sulphur dioxide compete for the hydrogen sulphide.²

The reduction of ferric chloride solutions by sulphur dioxide is utilised in both qualitative and quantitative analysis, but reduction is not complete in the presence of considerable excess of hydrochloric or sulphuric acid.³ Experiments show that ferrous chloride is oxidised by sulphur dioxide in concentrated hydrochloric acid solution in accordance with the equation :



Under the most favourable conditions the highest percentage of ferric iron obtained is 8.8. The degree of oxidation is independent of the initial concentration of total iron. It has also been shown that oxidation by sulphur dioxide at 95° C. does not occur in solutions of ferrous chloride unless there are present at least 165 grams of "free" HCl per litre.

Ferric chloride in concentrated hydrochloric acid solution is reduced by sulphur to a slight extent. Solutions containing more than 18.3 per cent. of ferric iron in the presence of 33 per cent. of hydrochloric acid are slowly reduced when a mixture containing equal quantities by weight of sulphur dioxide and hydrogen chloride is passed in at 115° C. From consideration of these facts it has been assumed that the reaction



is reversible.

The dependence of sulphur dioxide as an oxidising agent on a high concentration of hydrogen chloride has led to the suggestion that hydrogen chloride and sulphur dioxide first interact to a slight extent, forming thionyl chloride. Evidence in support of this is supplied by the following reactions with the mercaptans :

¹ Stewart and Wardlaw, *Trans. Chem. Soc.*, 1922, 121, 1481; Smythe and Wardlaw, *Proc. Durham Phil. Soc.*, 1913-14, 5, 187; Sartorius, *Annalen*, 1855, 96, 335; Sanders, *Zeitsch. angew. Chem.*, 1915, 28, 9.

² Durrant, *Trans. Chem. Soc.*, 1915, 107, 622.

³ Wardlaw, *J. Soc. Chem. Ind.*, 1926, 45, 210 T.

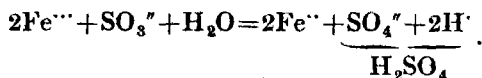


and



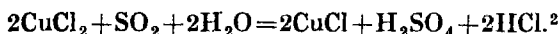
The fact that sulphur dioxide reduces most easily in a very dilute acid medium and oxidises most readily in a strongly acid medium may be correlated by explaining oxidation and reduction on an ionic basis, oxidation being represented by the surrender of positive charges and reduction by the transference of negative charges.

In aqueous solution sulphurous acid ionises into H^+ , HSO_3^- and SO_3^{--} ions. In this condition it acts as a reducing agent. Thus :

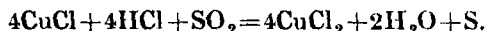


In strongly acid solution the concentration of SO_3^{--} ions is reduced and hence there is less tendency for reduction to take place.¹

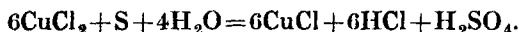
As in the case of ferric chloride, cupric chloride is only incompletely reduced by sulphur dioxide in concentrated hydrochloric acid solution, but in aqueous solution this forms an excellent method for the preparation of cuprous chloride :



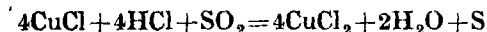
Experiment shows that cuprous chloride is oxidised in concentrated hydrochloric acid solution, thus :



It has also been shown that in the presence of concentrated hydrochloric acid sulphur can reduce a hot solution of cupric chloride in accordance with the equation :



It is believed that the reaction



is reversible, but that the reversibility is normally obscured by the reaction between the sulphur and cupric chloride in the presence of the hydrochloric acid.

Sulphur dioxide and sulphurous gases attack basic rocks and glasses superficially at high temperatures (900° C.) with the formation of water-soluble sulphates, chiefly sodium sulphate.² It is probable that such reaction and the solution of the products in hot springs during the early post-volcanic period explain the origin of alkaline sulphated thermal waters.

The capacity of sulphur dioxide to act either as an oxidising or as a reducing agent has been studied electrochemically in the case of

¹ Wardlaw, *J. Soc. Chem. Ind.*, 1926, 45, 210 T. For the action of sulphur dioxide on the chlorides of iron under various conditions and on molybdenum sulphate, see Wardlaw and Clews, *loc. cit.*; Wardlaw, Carter and Clews, *loc. cit.*; Wardlaw and Sylvester, *Trans. Chem. Soc.*, 1923, 123, 969.

² Wardlaw, *loc. cit.*

³ Portevin *Compt. rend.* 1928 187 1148.

solutions containing ferrous and ferric ions.¹ Results show that an increase in acid concentration is accompanied by a rise in the sulphur dioxide potential, whilst under the same conditions there is a diminution in the ferric-ferrous iron potential. Experiments on the cathodic reduction of sulphur dioxide in acid solution show that hydrogen sulphide is not formed as a primary product.

Many sulphides, both natural and artificial, react with sulphur dioxide at high temperatures with formation of the corresponding sulphate and sulphur, thus :



In the case of the alkali and alkaline earth metals, the sulphate is the sole product; with copper, lead, bismuth and antimony, the product contains the metal, formed by reduction of the sulphate by unchanged sulphide. In cases where the sulphate is unstable at the temperature of reaction, as with zinc, cadmium, aluminium, tin, chromium, iron, cobalt and nickel, the oxide is the final product. The action may be catalytically accelerated by the addition of triferric tetroxide, Fe_3O_4 .²

Sulphur Dioxide as an Unsaturated Reagent.—Sulphur dioxide exhibits a group of additive reactions indicative of its unsaturated nature.

Chlorine combines with the gas when the mixture is exposed to sunlight or when the sulphur dioxide is employed in solution in acetic acid or in camphor, the product being sulphuryl chloride;³ no combination occurs in the dark in the absence of a catalyst. In the presence of water the products are sulphuric acid and hydrochloric acid.⁴ Bromine does not combine in this manner, nor does hydrogen chloride, the freezing-point curve of the latter with sulphur dioxide showing only the formation of a eutectic mixture.⁵

Sulphur dioxide combines with oxygen to form sulphur trioxide; reaction occurs when the gaseous mixture is passed over certain porous substances, such as sugar charcoal, finely divided platinum, or certain oxides, for example, iron, copper or cobalt oxide (see p. 136). The rate of reaction is practically independent of the concentration of oxygen, but is proportional to that of the sulphur dioxide and inversely proportional to that of the trioxide.⁶ The mode of action of such "contact substances" is not clearly understood, although it is probable that the effect is due, at least in part, to a primary condensation of one or both of the reagents on the catalyst.⁷ Traces of moisture are necessary to the reaction.⁸ Hargreave's process for the conversion of sodium chloride into sodium sulphate is an interesting application of "contact

¹ Carter and James, *Trans. Chem. Soc.*, 1924, 125, 2231; Carter, *J. Soc. Chem. Ind.*, 1926, 45, 210 T.

² Milbauer and Tucek, *Chem. Zeit.*, 1926, 50, 323; Wohler, Martin and Schmidt, *Zeitsch. anorg. Chem.*, 1923, 127, 273. See also Henderson and Weiser, *J. Amer. Chem. Soc.*, 1913, 35, 239; Debus, *Trans. Chem. Soc.*, 1888, 53, 278; Berthier, *Annalen*, 1833, 5, 246; Delffs, *Jahresber.*, 1851, p. 174.

³ Melsens, *Compt. rend.*, 1873, 76, 92; Schulze, *J. prakt. Chem.*, 1881, 24, 168; Smits and de Mooy, *Proc. K. Akad. Wetensch. Amsterdam*, 1910, 13, 339.

⁴ This reaction has recently been investigated by Neumann and Wilczewski, *Zeitsch. angew. Chem.*, 1923, 36, 377.

⁵ Baume and Pamfil, *Compt. rend.*, 1911, 152, 1095.

⁶ Bodenstein and Fink, *Zeitsch. physikal. Chem.*, 1907, 60, 1, 45.

⁷ Keppeler, *Zeitsch. angew. Chem.*, 1908, 21, 532, 577.

⁸ Russell and Smith, *Proc. Chem. Soc.*, 1900, 16, 41.

oxidation" of sulphur dioxide, in which the sodium chloride itself acts as the contact substance. A current of steam, sulphur dioxide and air is passed over the heated salt; if a little iron oxide or copper oxide be mixed with the salt, a quantitative conversion may be effected at 500°C .¹

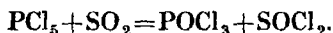
Peroxides, dioxides and many basic oxides react, often vigorously, with sulphur dioxide, forming the corresponding sulphate as one of the products of the reaction, the actual change in each case varying with the nature of the metal.² Sodium peroxide burns brilliantly when sprinkled into the gas. Lead dioxide becomes incandescent, whilst manganese dioxide reacts readily in the presence of water, the resulting solution containing dithionate and sulphate in addition to sulphite. Hydrogen peroxide gradually yields sulphuric acid.³

Another indication of the unsaturated nature of sulphur dioxide is given by its action on the alkali iodides and thiocyanates. Complexes of the type $\text{MI} \cdot x\text{SO}_2$ are obtained, where M is an alkali metal.⁴

Many aromatic hydrocarbons, for example, benzene, ethylbenzene, toluene, cymene and tetrahydronaphthalene, yield additive compounds.⁵ Such are also formed with liquid cyclic hydrocarbons in the absence of moisture and phenols, and use has been made of this fact to remove sulphur dioxide from a dry gas containing it.⁶ Additive compounds are also formed with methyl alcohol, thus $\text{CH}_3\text{OH} \cdot \text{SO}_2$ and $2\text{CH}_3\text{OH} \cdot \text{SO}_2$, the existence of which has been demonstrated definitely by means of the freezing-point curve.⁷ The additive compound with camphor has already been mentioned (p. 109).

Sulphur dioxide reacts with ammonia yielding *amidodisulphinic acid*, $\text{NH}_2 \cdot \text{SO}_2\text{H}$, which, in the presence of excess of ammonia, is accompanied by the ammonium salt together with a red substance, *triammonium imidodisulphinate*, $\text{NH}_4 \cdot \text{N}(\text{SO}_2 \cdot \text{NH}_4)_2$.⁸

Sulphur dioxide forms a substitution product in its reaction with phosphorus pentachloride, the products being thionyl chloride and phosphorus oxychloride :⁹



Sulphur Dioxide as a Reducing Agent.—When treated in a current of sulphur dioxide, nitrates are reduced, with formation of nitrous gases and sulphates; chlorates likewise are reduced, chlorine peroxide being obtained below 60°C ., whilst above this temperature the volatile products are sulphur trioxide and chlorine.

¹ Schultze, *J. prakt. Chem.*, 1880, [ii.], 21, 407; Krutwig, *Rec. Trav. chim.*, 1897, 16, [ii.], 173. For the action of the silent electric discharge on a mixture of sulphur dioxide and oxygen, see p. 137.

² Hammick, *Trans. Chem. Soc.*, 1917, 111, 379.

³ Russell and Smith, *Proc. Chem. Soc.*, 1900, 16, 41. See also Mayer, *Ber.*, 34, 3606. For the action of SO_2 on NO_2 , see p. 250.

⁴ de Forcrand and Taboury, *Compt. rend.*, 1919, 168, 1253; 169, 162; Ephraim and Kornblum, *Ber.*, 1916, 49, 2007; Adrianowski, *ibid.*, 1879, 12, 688; Pèchard, *Compt. rend.*, 1900, 138, 1188.

⁵ de Carh, *Atti R. Accad. Lincei*, 1926, [vi.], 4, 460, 523; Mazzetti and de Carli, *Gazzetta*, 1926, 56, 34.

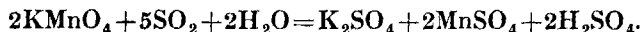
⁶ Howard, *U.S. Patent*, 1606299 (1926).

⁷ Baume and Pamfil, *loc. cit.*

⁸ Ephraim and Piotrowski, *Ber.*, 1911, 44, 379; Ogawa and Aoyama, *Sci. Reports Tôhoku Imp. Univ.*, 1913, 2, 121; Divers and Ogawa, *Proc. Chem. Soc.*, 1900, 16, 38.

⁹ Schiff, *Annalen*, 1857, 102, 111.

Chromates and permanganates are vigorously reduced.¹ Thus, on passing a current of sulphur dioxide through an acidified aqueous solution of potassium dichromate, reduction to chromium sulphate occurs, the orange solution becoming purple-green and depositing, upon concentration, crystals of potassium-chromium alum. Permanganates react similarly, the manganese being reduced to manganous sulphate and the solution becoming practically colourless. Thus :



This reaction is the basis of a useful volumetric method of estimating sulphites in solution (see p. 129).²

Physiological Action.—Sulphur dioxide exerts a decidedly toxic effect on plants³ and animals,⁴ and has been used in poison gas warfare (see p. 106); even as little as 0.04 per cent. by volume in the atmosphere will cause symptoms of poisoning in human beings after a few hours; in larger quantities, either gaseous or dissolved, the effect may be fatal. The gas acts as a direct blood poison and also affects the blood circulation.⁵ The sulphites are not poisonous.⁶

Applications.—Gaseous sulphur dioxide is used for bleaching certain natural colours, e.g. in wool, silk, feathers, straw and sugar; its action is less powerful than that of chlorine and some yellow flowers are unaffected by it.⁷ In some cases the bleaching, which occurs in the presence of moisture, is probably due to a reducing action, but for the most part the colour, for example, with red rose petals, can be restored partly by warming or treating with dilute sulphuric acid; the bleaching in the latter case is probably due, at least partially, to the formation of a feeble compound between the sulphur dioxide and the pigment.

The disinfectant action⁸ of sulphur dioxide was recognised by the ancient Greeks and is mentioned by Homer. To-day the gas is less favoured than in the past as a disinfectant although it is still largely used; it is also applied, more generally in the form of sulphite, for preservative purposes. Fresh whole fruit may be preserved in sealed vessels in an aqueous solution containing 0.08 to 0.1 per cent. of sulphur dioxide: ⁹ absorption by the fruit occurs and the concentration falls to 0.04 per cent., but the growth of micro-organisms is inhibited, and jam made from such fruit is said to be of superior quality to that made from pulp. The application of sulphur to vines for the prevention of

¹ Hodgkinson and Young, *Chem. News*, 1892, 66, 199.

² For the action of sulphur dioxide on manganic hydroxide, see Meyer and Schramm, *Zeitsch. anorg. Chem.*, 1923, 132, 226.

³ Wieler, *Ber. Deut. bot. Ges.*, 1903, 20, 656; *Naturw. Rundschau*, 1907, 22, 229; Schroder, *Dingl. poly. J.*, 1873, 207, 87; Winkler, *Zeitsch. angew. Chem.*, 1896, p. 370.

⁴ Ogata, *Arch. Hygiene*, 1884, 2, 223; Pfeiffer, *Arch. exp. Path. Pharm.*, 1890, 27, 261; Lehmann, *Arch. Hygiene*, 1893, 18, 180; Walbaum, *ibid.*, 1906, 57, 87; Jacobi and Walbaum, *Arch. exp. Path. Pharm.*, 1906, 54, 1421; Grunhut, *Biochem. Zeitsch.*, 1908, 11, 29; König and Hasenbaumer, *Bied. Centr.*, 1903, 32, 535.

⁵ Kionka, *Zeitsch. Hygiene*, 1896, 22, 351.

⁶ Ogata, *loc. cit.*

⁷ Schroder, *loc. cit.* See also Hird and Lloyd, *J. Soc. Chem. Ind.*, 1912, 31, 317; Spring, *Bull. Acad. roy. Belg.*, 1881, [iii.], 1, 2; Schulze, *Dingl. poly. J.*, 1871, 200, 231; Pictet, *Chem. Zeit.*, 1895, 19, 425.

⁸ Calvert, *Proc. Roy. Soc.*, 1872, 20, 187; Baierlacher, *Dingl. poly. J.*, 1877, 224, 458; Wernich, *Ber.*, 1879, 12, 1705; Fatio, *Compt. rend.*, 1880, 90, 851; Brühl, *ibid.*, 1889, 108, 824; Hatton, *Trans. Chem. Soc.*, 1881, 39, 247.

⁹ Barker and Grove, *J. Pomology*, 1925, 5, 50.

disease possibly owes its efficiency to a very slow formation of sulphur dioxide (see, however, p. 12).

Liquid sulphur dioxide finds occasional use as a refrigerating liquid for the manufacture of ice and as a solvent for the extraction of fats and oils from bones and other waste animal matter. It is also employed in the refining of natural petroleum, owing to its property of dissolving aromatic and other heavy hydrocarbons which are present in petroleum distillates.¹ When the distillate is shaken with liquid sulphur dioxide at a low temperature, separation into two layers occurs, one of which is the sulphur dioxide solution, the other the purified distillate containing paraffin hydrocarbons and naphthenes, which remain unaffected.

The gas is used in various chemical industries. For example, it forms an intermediate stage in the production of sulphuric acid and of sulphites; it is also applied in the preparation of chemical substances such as selenium, tellurium, quinol, etc. To some extent sulphur dioxide finds application for fire-prevention and -extinguishing, and much is used in the form of alkali sulphite in the production of wood pulp for paper and artificial silk manufacture.

Detection and Estimation.—The detection of sulphur dioxide, except by its odour and a few special reactions such as its reduction to hydrogen sulphide by hydrogen (p. 115) and its reducing action on potassium chromate paper, is generally effected by the same tests as are applied to the dissolved gas (p. 128). The gas may also be recognised by lowering into it a rod which has been thinly coated with a layer of moist zinc nitroprusside, rendered transparent by exposure to ammonia. According to the amount of sulphur dioxide present the coating turns rose or deep red in colour.² The addition of pure zinc to a solution of sulphurous acid causes reduction to hydrosulphite, which may be detected by its action on Methylene Blue.³

Sulphur dioxide is conveniently estimated volumetrically by absorption in sodium hydroxide solution and, after acidifying with hydrochloric acid, titrating the solution with potassium iodate.⁴ Direct titration of sulphur dioxide solutions does not give consistent results except under special conditions.⁵ The solution should be made strongly alkaline and a small amount of sugar added; it is then put into a burette and run into a definite quantity of standard iodine solution made strongly acid with hydrochloric acid. For the accurate determination of small amounts of sulphur dioxide in gaseous mixtures the excess of iodine method is recommended. In this method the sulphur dioxide is dissolved directly in excess of iodine and the excess determined by means of thiosulphate and starch.⁶ Oxidation with permanganate under definite conditions (see p. 129) is a usual method for estimation of the gas, permanganate solution being more stable than iodine solution.⁷ A method of estimating sulphur dioxide in a solution of bisulphite by the addition of mercuric chloride and subsequent

¹ Edeleanu, *British Patent*, 11140 (1908). See Campbell, *Petroleum Refining*, pp. 180 *et seq.* (C. Griffin & Co., 1922); also Brandt, *Ind. Eng. Chem.*, 1930, 22, 218.

² Eegriwe, *Zeitsch. anal. Chem.*, 1924, 65, 182.

³ Noll, *Farben Ztg.*, 1928, 33, 1849.

⁴ Haller, *J. Soc. Chem. Ind.*, 1919, 38, 52 T. See also Ries and Clark, *Ind. Eng. Chem.*, 1926, 18, 747.

⁵ Maass and Maass, *J. Amer. Chem. Soc.*, 1928, 50, 1352.

⁶ Ferguson, *ibid.*, 1917, 39, 364.

⁷ Sweeney, Outoault and Withrow, *J. Ind. Eng. Chem.*, 1917, 9, 949.

titration with sodium hydroxide solution is described by Debucquet.¹ For the estimation of sulphur dioxide in wines, the wine is heated for some time with excess of sodium hydroxide solution, and the excess alkali then neutralised with dilute sulphuric acid and the solution titrated with iodine and starch.²

Formula and Constitution.—From the fact that when sulphur is burnt in oxygen the volume of sulphur dioxide obtained is approximately equal to the original volume of the oxygen, it is obvious that a molecule of sulphur dioxide must contain one molecule or two atoms of oxygen; this observation, together with the fact that the vapour density of sulphur dioxide approximates to 32, supplies sufficient evidence for the molecular formula SO_2 .

Rankine and Smith³ have employed the method of determination of the molecular dimensions of gaseous molecules from viscosity measurements to decide the constitution of the sulphur dioxide molecule. From

their results they deduce that the molecule has the structure $\text{S} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array}$, rather than $\text{O}=\text{S}=\text{O}$, proposed by Langmuir.⁴

Sulphurous Acid.

Formation.—Sulphur dioxide imparts to water acidic properties, owing to the formation of an unstable sulphurous acid; the chemical properties of moist or dissolved sulphur dioxide are therefore very largely the properties of sulphurous acid.

By analogy with the corresponding salts the acid should possess a formula H_2SO_3 , but the substance has not been isolated, the solutions decomposing and yielding free sulphur dioxide even when allowed to evaporate at the ordinary temperature. A number of solid products described as *hydrates* of the acid have been obtained (see p. 109); they are best produced by the prolonged passage of sulphur dioxide into water at about 0°C ., when a crystalline deposit slowly forms. The products are easily dissociable, denser than water, and have melting-points not far removed from 4°C . It has been shown, however, that only one hydrate, $\text{H}_2\text{SO}_3 \cdot 5\text{H}_2\text{O}$,⁵ exists, and that the other products are to be regarded as mixtures of this hydrate with ice.

It is worthy of note that liquid sulphur dioxide and water are not completely miscible at low temperatures.⁶

Properties.—Sulphur dioxide dissolves in water with the evolution

¹ Debucquet, *J. Pharm. Chim.*, 1924, [vu.], 29, 66.

² Marcille, *Ann. Falsif.*, 1922, 15, 398. For the determination of sulphur dioxide in sugars and sugar factory products, see Baissac, *Int. Sugar J.*, 1927, 29, 538; Ogilvie, *ibid.*, 1926, 28, 644; Hurst, *Trop. Agric.*, 1927, p. 66; in dried fruit, see May, *Analyst*, 1927, 52, 271, also p. 526; cf. Miller, *ibid.*, p. 338; in foods, see Black and Warren, *ibid.*, 1928, 53, 130; Jones, *ibid.*, p. 138, also p. 118; Henville, *ibid.*, 1929, 54, 228; in fatty substances, see Knapp and Phillips, *ibid.*, 1928, 53, 149; in the atmosphere, see McKay and Ackerman, *Ind. Eng. Chem.*, 1928, 20, 538; Thomas and Cross, *ibid.*, p. 645; Thomas and Abersold, *ibid. (Anal.)*, 1929, 1, 14; in flue gases, see Nestell and Anderson, *J. Ind. Eng. Chem.*, 1916, 8, 258; in bleaching (tannin) extracts, see Burton and Charlton, *J. Soc. Leather Trades Chem.*, 1926, 10, 326.

³ Rankine and Smith, *Proc. Physical Soc.*, 1922, 35, 33. See also Ghosh and Mahanti, *Physikal. Zeitsch.*, 1929, 30, 531.

⁴ For further discussion of the constitution, see Friend, *Proc. Chem. Soc.*, 1909, p. 91.

⁵ Tammann and Krige, *Zeitsch. anorg. Chem.*, 1925, 146, 179.

⁶ Baume and Tykociner, *J. Chim. phys.*, 1914, 12, 270.

of heat (p. 107). The aqueous solutions are denser than water.¹ The ready decomposition of sulphurous acid is obvious from the pungent smell of sulphur dioxide always observable above the solution.

The acid is rather feeble, but it reddens litmus,² decomposes carbonates and neutralises alkalis with the formation of salts. The baser metals are also slowly attacked, and the liquid finds frequent use as an etching reagent in the metallographic examination of alloys.³

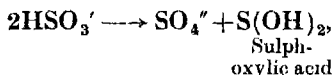
Although the solution conducts the electric current,⁴ the dissolved sulphur dioxide is mainly in an un-ionised condition and even unhydrated;⁵ what electrolytic dissociation does occur is mainly into the ions H^+ and HSO_3' , the proportion of SO_3'' ions being very small indeed.⁶

The absorption spectra of the aqueous solutions indicate that the sulphur dioxide is mainly present as SO_2 molecules, some hydrate molecules also being present, but only small amounts of H_2SO_3 and its ions.⁵

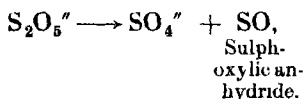
Autoxidation.—Aqueous solutions of sulphurous acid are well known to undergo slow autoxidation in the absence of air or oxidising agents, the change being usually represented by the equation:



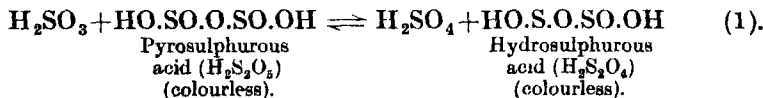
This change is accelerated by rise of temperature and by exposure to light.⁷ It has been suggested⁸ that the following initial reactions are involved:



and/or



the sulphylic acid (or its anhydride) undergoing subsequent change, ultimately yielding sulphuric acid and sulphur. Bassett and Durrant⁹ consider the initial reaction to be:



¹ Carius, *Annalen*, 1855, 94, 148; Bunsen and Schönfeld, *ibid.*, 1855, 95, 2; Sims, *ibid.*, 1861, 118, 340; Giles and Shearer, *J. Soc. Chem. Ind.*, 1885, 4, 303; Porman, *Trans. Chem. Soc.*, 1895, 67, 897; Eversheim, *Physikal. Zeitsch.*, 1903, 4, 503.

² Thomsen, *Chem. News*, 1883, 47, 123, 135, 184.

³ Hilpert and Colvert-Glauert, *Zeitsch. anorg. Chem.*, 1910, 68, 63.

⁴ Ostwald, *J. prakt. Chem.*, 1885, [ii.], 32, 314; Drucker, *Zeitsch. physikal. Chem.*, 1904, 49, 579; Bouty, *Compt. rend.*, 1884, 99, 31.

⁵ Garrett, *Trans. Chem. Soc.*, 1915, 107, 1324; Wright, *ibid.*, 1914, 105, 699, 2907; Dietzel and Galanos, *Zeitsch. Elektrochem.*, 1925, 31, 486.

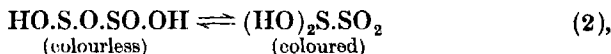
⁶ Drucker, *loc. cit.*; Jellinek, *Zeitsch. physikal. Chem.*, 1911, 76, 257; Kerp and Bauer, *Chem. Zentr.*, 1907, ii., 971; Landner, *Monatsh.*, 1912, 33, 613.

⁷ Loew, *Amer. J. Sci.*, 1870, [ii.], 49, 368; *Jahresber.*, 1873, p. 164; Berthelot, *Ann. Chim. Phys.*, 1898, [vii.], 14, 289.

⁸ Foerster, Lange, Drossbach and Seidel, *Zeitsch. anorg. Chem.*, 1923, 128, 268.

⁹ Bassett and Durrant, *J. Chem. Soc.*, 1927, p. 1401.

It is pointed out that although aqueous sulphurous acid appears to contain most of its sulphur dioxide as such,¹ yet solutions of the alkali bisulphites appear to contain some pyrosulphite (metabisulphite).² It is therefore not unreasonable to assume that some free pyrosulphurous acid is present in aqueous sulphurous acid solutions. Since hydro-sulphurous acid is unstable under the prevailing conditions, it does not accumulate, but rapidly undergoes further change, which makes proof of its formation difficult. It is assumed³ that some of the colourless acid formed in reaction (1) undergoes rearrangement to the isomeric coloured form :



and that these two isomerides react, yielding pyrosulphurous and thio-sulphuric acids, thus :



The thiosulphuric acid now undergoes further change (see p. 195), one of the first products being trithionic acid, $\text{H}_2\text{S}_3\text{O}_6$, tetra- and penta-thionic acids being gradually formed as the concentration of sulphurous acid diminishes with the progress of autoxidation. These acids in their turn gradually decompose, the final products being sulphuric acid and free sulphur. This explains why thionic acids are almost always present in old solutions of sulphurous acid, whether these have been entirely protected from atmospheric oxidation or not, and the amount of these acids present will depend largely upon the age and composition of the solution.

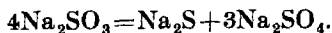
It must be stated, however, that the absorption spectra of aqueous alkali hydrogen sulphite solutions are similar to those of sulphur dioxide, and even aqueous or alcohol solutions of potassium or ammonium pyrosulphite show no spectrum characteristic of the ion $\text{S}_2\text{O}_5^{2-}$. On warming or on exposure to light, such solutions show an increased absorption, the bands being displaced towards the longer wave-lengths, and this is to be explained by the photo-oxidation of HSO_3^- ions to SO_4^{2-} , with formation of SO_2 -hydrate.⁴

Dilute solutions of sulphurous acid decompose more quickly and completely than concentrated solutions, while in presence of a strong acid the decomposition is inhibited, being completely suppressed in twice-normal hydrochloric acid solution.

It has been found that sulphurous acid liberated in solution from its salts at temperatures of 100° to 120° C. or lower, may undergo instantaneous *auto-reduction* with production of hydrogen sulphide :



this corresponding with the change which takes place when solid sodium sulphite is heated above 150° C. :



It appears, moreover, that this rapid auto-reduction occurs only with sulphurous acid liberated from its salts and not with gaseous sulphur

¹ Wright, *Trans. Chem. Soc.*, 1914, 105, 2907.

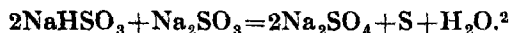
² Baly and Bailey, *ibid.*, 1922, 121, 1813; Getman, *J. Physical Chem.*, 1926, 30, 266.

³ Bassett and Durrant, *loc. cit.*

⁴ Dietzel and Galanos, *loc. cit.*

dioxide or saturated solutions of the gas or even with the solid hydrate. It seems possible that the high reducing power of the sulphurous acid under these conditions may be due to the momentary existence of the acid $\text{H}\cdot\text{SO}_2\cdot\text{OH}$, produced from a corresponding metallic salt such as was postulated by Divers and Shimidzu.¹

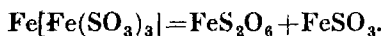
A mixture of sodium sulphite and sodium hydrogen sulphite in aqueous solution at 150°C . undergoes a change in accordance with the equation:



Electrolysis of sulphurous acid causes anodic oxidation to sulphuric acid, whilst hydrosulphurous acid, $\text{H}_2\text{S}_2\text{O}_4$, is produced by the reducing action of the current at the cathode;² the former change may be rendered quantitative by the addition of a manganese salt;³ the hydrosulphurous acid may be accompanied by various of its decomposition products.⁵

The most marked group of reactions exhibited by sulphurous acid is dependent on its reducing power. In dilute aqueous solution slow oxidation by free oxygen occurs⁶ with liberation of 63.6 Cals. per gram-molecule oxidised;⁷ the change is accelerated by the influence of light and the presence of salts of manganese, cobalt or iron.⁸ Sulphurous acid solution reduces selenious and tellurous acids to selenium and tellurium, respectively; it precipitates the noble metals, for example gold, from solutions of their salts. Salts derived from higher oxides are generally reduced to derivatives of lower oxides; thus ferric salts, chromates, manganates and permanganates (see p. 121) yield ferrous, chromic and manganous salts, respectively.

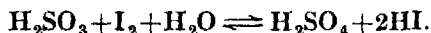
In the case of the reduction of ferric salts by sulphur dioxide it has been suggested⁹ that the reduction most probably proceeds in stages, a red ferric ferrisulphite, $\text{Fe}[\text{Fe}(\text{SO}_3)_3]$, being first formed, which on warming yields the ferrous salt and the dithionate, thus:



On boiling, the dithionate decomposes:



The halogen elements are converted into the corresponding hydracids by sulphurous acid, the change being reversible in the case of bromine and especially with iodine:



In this reaction it has been shown that there is an intermediate formation of a yellow compound of composition $\text{SO}_2\cdot\text{HI}$.¹⁰

¹ Divers and Shimidzu, *Trans. Chem. Soc.*, 1886, 49, 577; Bennett, *Trans. Chem. Soc.*, 1922, 121, 1794.

² Bayer & Co., *German Patent*, 265167 (1913).

³ Guérout, *Compt. rend.*, 1877, 85, 225. See also Luckow, *Zeitsch. anal. Chem.*, 1880, 19, 1.

⁴ See Fischer and Demarcel, *Bull. Soc. chim. Belg.*, 1910, 24, 236.

⁵ Thompson, *Met. and Chem. Eng.*, 1916, 15, 677.

⁶ Reese, *Ber.*, 1884, 17, 588.

⁷ Thomsen, *Ber.*, 1873, 6, 1438.

⁸ Meyer, *Ber.*, 1887, 20, 3058. See also Berg, *Compt. rend.*, 1904, 138, 907.

⁹ Meyer, *Ber.*, 1920, 53, [B], 77.

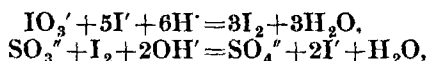
¹⁰ Macaulay, *Trans. Chem. Soc.*, 1922, 121, 552.

In an analogous manner cyanogen, which in many of its reactions exhibits a marked similarity to chlorine, is slowly reduced to hydrocyanic acid : ¹



cyanogen iodide, CNI, in like manner gives hydrocyanic and hydriodic acids. ²

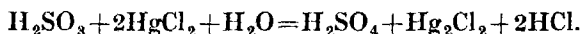
With the exception of perchloric acid, the halogen oxyacids are reduced through the corresponding halogen elements to the hydracids; in the case of iodic acid ³ the formation of free iodine after a definite interval forms a striking example of a "time reaction." ⁴ The formation of the element is not observed until after the disappearance of the whole of the sulphite. The mechanism of the reaction is probably as follows :



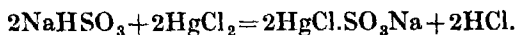
the latter reaction being much more rapid than the former.

Nitric acid ⁵ undergoes reduction by sulphurous acid less readily than nitrous acid, ⁶ the product in each case being sulphuric acid with nitrous or nitric oxide: it is possible that nitrogen-sulphur acids such as nitro-sulphonic acid are intermediately produced (see p. 248). Nitric oxide can be reduced slowly to nitrous oxide by sulphurous acid, but no further. ⁷

Mercuric chloride readily oxidises sulphurous acid, the reaction being quantitative if the solution of the latter is dilute :



The result is different if sodium hydrogen sulphite is used instead of sulphurous acid; the addition of excess of mercuric chloride then gives rise to an equimolecular proportion of hydrochloric acid, the titration of which provides a convenient method for estimating the quantity of hydrogen sulphite originally present : ⁸



By taking a sulphurous acid solution and titrating with sodium hydroxide and methyl orange until the sodium hydrogen sulphite is formed, then adding excess of mercuric chloride and completing the titration, sulphurous acid itself may be estimated.

¹ Vorlander, *Verh. Ges. deut. Naturforsch. Aerzte*, 1907, 11., 92.

² Meimeke, *Zeitsch. anorg. Chem.*, 1892, 2, 157. This reaction may be used for the determination of sulphites, see Alsterberg, *Biochem. Zeitsch.*, 1926, 172, 223.

³ See Vol. VIII. of this series, p. 240.

⁴ Landolt, *Ber.*, 1886, 19, 1340; 1887, 20, 745; Persoz, *Annalen*, 1847, 64, 408; Selmons, *Ber.*, 1888, 21, 230; Thiel, *Sitzungsber. Ges. Ford. Naturw. Marburg*, 1912, 2, 11; Patterson and Foreyth, *Trans. Chem. Soc.*, 1912, 101, 40; Skrabal and Zahorka, *Zeitsch. Elektrochem.*, 1927, 33, 42.

⁵ Raschig, *Zeitsch. angew. Chem.*, 1905, 18, 1302.

⁶ Weber, *Ann. Phys. Chem.*, 1866, 127, 277, 543; Frémy, *Compt. rend.*, 1870, 70, 61; Raschig, *Ber.*, 1887, 20, 584, 1158; *Zeitsch. angew. Chem.*, 1904, 17, 1398.

⁷ Pelouze, *Ann. Chim. Phys.*, 1835, 60, 162; Weber, *loc. cit.*; Lunge, *Ber.*, 1881, 14, 2196.

⁸ Sander, *Zeitsch. angew. Chem.*, 1915, 28, 9; 1916, 29, 11, 16; *Chem. Zeit.*, 1915, 39, 945.

The compound obtained by the interaction of mercuric chloride and ammonia dissolves when sulphur dioxide is passed through the liquid.¹

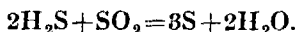
Sulphurous acid can, on the other hand, undergo reduction. Hydrogen sulphide reduces it, producing sulphur chiefly. The primary action may be represented by the reversible equation :



The compound H_2SO , which is assumed to be of the peroxide type, decomposes with precipitation of sulphur. The hydrogen sulphide also reacts further with the sulphylic acid primarily formed to yield more H_2SO :

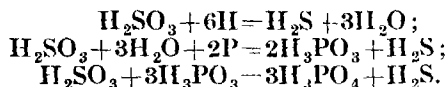


so that the final result of the interaction is



This final stage is reached more quickly in the presence of excess of hydrogen sulphide. In the presence of excess of sulphurous acid some polythionic acid is formed.²

Phosphorus at 200° C. in a sealed tube gives phosphoric acid and hydrogen sulphide.³ Nascent hydrogen, for example from zinc and sulphuric acid, yields hydrogen sulphide,⁴ as also do phosphorous acid,⁵ titanous chloride, and even stannous chloride :⁶



Formic acid gives a reducing action of an unusual type with sulphurous acid ; the mixture of the two acids is a much stronger reducing agent than either of the components by itself, on account of the formation of hydrosulphurous acid :



Hydrosulphurous acid is also formed by the action of many metals on sulphurous acid ;⁷ the crust of ferrous sulphite and hydrosulphite formed on the surface of metallic iron is of great protective value in the iron cylinders used for storing liquid sulphur dioxide, which generally contains traces of water.⁸

Detection and Estimation.—Sulphurous acid is usually detected by its reducing action, for instance on potassium dichromate solution, the acid being warmed in order that the test may be effected with the evolved gas ; the odour of sulphur dioxide is also a fairly trustworthy indication. For special purposes⁹ many of the reactions already mentioned may be applied.

¹ Ruff, Krohnert and Braun, *Zeitsch. anorg. Chem.*, 1920, **114**, 203.

² Heinze, *J. prakt. Chem.*, 1919, [u.], **99**, 109.

³ Oppenheim, *Bull. Soc. chim.*, 1864, [ii.], **1**, 163.

⁴ Berthelot, *Ann. Chim. Phys.*, 1898, [vii.], **14**, 289.

⁵ Wöhler, *Annalen*, 1841, **39**, 252. See also Schonbein, *J. prakt. Chem.*, 1853, **61**, 193.

⁶ Wackenroder, *Pharm. Centr.*, 1846, p. 615 ; Muir, *Mon. scient.*, 1882, [iii.], **12**, 783 ; Donath, *Zeitsch. anal. Chem.*, 1897, **36**, 663 ; Fedorow, *Zeitsch. Chem.*, 1869, **5**, 15 ; Durrant, *Trans. Chem. Soc.*, 1915, **107**, 622 ; Smythe and Wardlaw, *Proc. Durham Phil. Soc.*, 1913–14, **5**, 187.

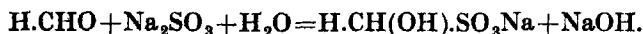
⁷ Schweitzer, *Chem. News*, 1871, **23**, 293 ; Lange, *Zeitsch. angew. Chem.*, 1899, **12**, 275, 300.

⁸ Lange, *loc. cit.*

⁹ For the detection of sulphites in foodstuffs, see Parkes, *Analyst*, 1926, **51**, 620. See also p. 123, footnote 2.

A sensitive colour test for sulphite ions consists in adding, drop by drop, a 0.01 per cent. solution of Fast Blue R crystals, shaking after each addition, until the violet coloration disappears and a yellow solution is produced; the test is sensitive to one part of sulphurous acid in about 175,000. Thiosulphates and polythionates do not interfere, but sulphides and hydroxides must be absent.¹

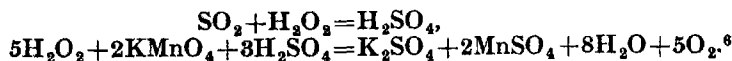
If to a neutral solution of an alkali sulphite containing phenolphthalein a few drops of a 1 per cent. formaldehyde solution are added, a pink colour due to liberation of alkali hydroxide is produced:²



When a solution containing sulphite is added to a few drops of Bettendorf's reagent (stannous chloride in concentrated hydrochloric acid) a yellowish-brown deposit of tin sulphides is formed, owing to reduction of the sulphite; 0.6 per cent. of the latter can thus be detected.³

Contrary to what might be expected, the estimation of sulphurous acid cannot be satisfactorily effected by direct titration with potassium permanganate in the presence of an acid, because, under ordinary conditions, a considerable proportion of the sulphurous acid escapes complete oxidation, being converted into dithionic acid.⁴ More satisfactory results are obtained by the addition of a large excess of permanganate (or dichromate) with sulphuric acid and the subsequent determination of the excess by a suitable standard solution, *e.g.* of oxalic acid or ferrous sulphate. Good results have been obtained by observing the following definite conditions. A known volume of acidified standard potassium permanganate solution is divided into two portions, one being reserved for comparison. To the other portion is added the sulphurous acid to be estimated, and more standard permanganate is added until the colour is again of the same intensity as that of the reserved portion. The solutions are mixed, divided into two portions and the process again repeated. These repetition operations are necessary owing to the fact that the colour obtained on re-titrating a mixture of sulphurous acid and potassium permanganate is slightly different in tint from that of the permanganate alone. The quantity of permanganate solution required to restore the standard colour is equivalent to the amount of sulphurous acid present.⁵

Another method which is applicable also to the estimation of solutions containing sulphites and hydrogen sulphites is the addition of a known excess of acidified hydrogen peroxide to the solution of sulphurous acid. The excess of peroxide may then be titrated with standard permanganate solution. The reactions are as follows:



¹ Eegriwe, *Zeitsch. anal. Chem.*, 1926, 69, 382.

² Rosenthaler, *Mikrochem.*, 1927, 5, 27.

³ Dunajeva, *Pharm. J. (Russia)*, 1928, p. 379; *Chem. Zentr.*, 1928, ii., 1129.

⁴ Péan de St. Gilles, *Ann. Chim. Phys.*, 1858, [iii.], 55, 374; Buignet, *J. Pharm. Chim.*, 1859, [iii.], 36, 122; Fordos and Gélis, *ibid.*, p. 113; Lunge and Smith, *J. Soc. Chem. Ind.*, 1883, 2, 460; Dymond and Hughes, *Proc. Chem. Soc.*, 1896, 175, 42; Milbauer, *Zeitsch. anal. Chem.*, 1909, 48, 17; Kolthoff, *Pharm. Weekblad*, 1924, 61, 841.

⁵ Barham, *Chem. News*, 1922, 124, 279; Sweeney, Outcault and Withrow, *J. Ind. Eng. Chem.*, 1917, 9, 949.

⁶ Craig, *J. Soc. Chem. Ind.*, 1919, 38, 96 T.

The more usual volumetric method for the estimation of sulphurous acid is the excess iodine method already described (p. 122).¹ The reaction between the acid and iodine is not reversible in the state of dilution obtaining in volumetric analysis, therefore the addition of sodium hydrogen carbonate, as often recommended, is unnecessary.² The low results obtained when the sulphurous acid is exposed to air during the titration are due entirely to evaporation of sulphur dioxide, the amount of atmospheric oxidation being negligible. Sulphite solutions, on the other hand, readily undergo atmospheric oxidation, so that in order to obtain an accurate estimation of sulphite it is advisable to dissolve the salt in a 5 per cent. recently boiled glycerol solution in a flask filled with carbon dioxide and then run in a measured excess of standard iodine solution also under carbon dioxide and titrate the residual iodine with thiosulphate.³ Satisfactory results may also be obtained by employing more powerful oxidising agents, such as an acid solution of potassium iodate,⁴ or sodium hypochlorite.⁵ In the latter case, excess of a standard hypochlorite solution is added to the sulphurous acid solution and titrated back with iodine. This method is applicable to solutions of high SO_2 -concentration.

It is also possible with sulphurous acid solutions, using methyl orange as indicator, to titrate with a standard solution of an alkali to the half-way "bisulphite" stage.⁶ If necessary the alkali hydrogen sulphite may then be estimated by the addition of mercuric chloride and further titration with alkali, as already described. By this double titration method it is possible to estimate sulphurous acid in the presence of other sulphur acids.⁷

Occasionally it is desired to determine sulphurous acid by a gravimetric method; it is then usual to expel the sulphur dioxide from the solution under examination by distilling in an atmosphere of carbon dioxide and oxidise the gas to sulphuric acid by absorption in bromine water or iodine solution, subsequently adding barium chloride and weighing the precipitated barium sulphate. This method also gives accurate results volumetrically if steps are taken to prevent loss of iodine by volatilisation in the current of carbon dioxide. The excess iodine is titrated with a solution of sodium thiosulphate.⁸

The Sulphites.—Sulphurous acid gives rise to normal sulphites of the type M_2SO_3 and acid salts of the type MHSO_3 , where M represents a univalent metal atom. The normal salts are odourless and do not resemble the free acid or sulphur dioxide in their very harmful effect on living organisms. On the other hand, the acid sulphites readily yield sulphur dioxide; they have an acid reaction towards phenolphthalein, but are neutral towards methyl orange.

¹ See also Kolthoff, *Pharm. Weekblad*, 1919, 56, 1366.

² Macaulay, *Trans. Chem. Soc.*, 1922, 121, 552.

³ Waterman, *Chem. Weekblad*, 1920, 17, 196. See also Mason and Walsh, *Analyst*, 1928, 53, 144.

⁴ Hendrixson, *J. Amer. Chem. Soc.*, 1925, 47, 1319, 2156; Bonner and Yost, *Ind. Eng. Chem.*, 1926, 18, 55.

⁵ Bioskei, *Zeitsch. anorg. Chem.*, 1927, 160, 64.

⁶ Lunge, *Zeitsch. angew. Chem.*, 1895, p. 221. See also Sander, *Chem. Zeit.*, 1914, 38, 1057.

⁷ Graire, *Compt. rend.*, 1924, 178, 1819. See also Kurténacker, *Zeitsch. anorg. Chem.*, 1924, 134, 265; *Zeitsch. anal. Chem.*, 1924, 64, 56.

⁸ Coppetti, *Ann. Chim. anal.*, 1921, 3, 327. For a bromometric method of determination of sulphurous acid, see Manchot and Oberhauser, *Ber.*, 1924, 57, [B], 29.

Other saline derivatives of sulphur dioxide are known corresponding with a hypothetical acid $\text{H}_2\text{S}_2\text{O}_5$; for example, alkali *metabisulphites* or *pyrosulphites* of the composition $\text{M}_2\text{S}_2\text{O}_5$ are known, which may be considered as structurally derived from two molecules of the hydrogen sulphites MHSO_3 by elimination of one molecule of water. They are well-defined compounds obtained by crystallisation from aqueous solutions of the sulphites of the alkali metals in the presence of excess of sulphur dioxide.¹

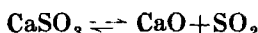
Sulphurous acid and the alkali sulphites show a marked tendency to react with sulphites of the heavier metals to form complexes in which the ordinary reactions of the heavy metal are often more or less obscured.²

The alkali sulphites and bisulphites are produced on the large scale by treating lime and magnesia or dolomitic limestone with sulphur dioxide in the presence of water, then adding the requisite amount of alkali sulphate to the filtrate and filtering off any insoluble sulphate;³ or, alkali carbonate or bicarbonate may be treated directly with sulphur dioxide.⁴

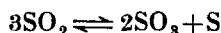
The action of heat on sulphites varies both with the temperature and with the nature of the metal concerned. With sodium sulphite, Na_2SO_3 , the chief reaction at 700°C. *in vacuo* is



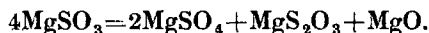
and apparently lithium sulphite behaves similarly.⁶ In the case of calcium sulphite an analogous reaction takes place at about 650°C. , but at 1100°C. the dissociation



is practically complete. The residue contains calcium sulphate in addition to the oxide, probably because the equilibrium



becomes effective at higher temperatures. Magnesium sulphite decomposes at 300°C. according to the equation:⁷



¹ Muspratt, *Annalen*, 1844, 50, 259; Berthelot, *Compt. rend.*, 1883, 96, 208; *Ann. Chim. Phys.*, 1884, [6], 1, 87; Carey and Hurter, *Ber.*, 1884, 17, 33; Rohrig, *J. prakt. Chem.*, 1883, [ii.], 37, 217; Geuther, *Annalen*, 1884, 224, 218. See also Bernthsen and Bazlen, *Ber.*, 1900, 33, 126; Besson, *Chem. Zeit.*, 1916, 40, 165.

² Such compounds will be found described under the various metals in other volumes of this series. For the preparation and properties of $\text{Li}_2\text{Co}(\text{SO}_3)_3 \cdot 4\text{H}_2\text{O}$, see Abresch, *Zeitsch. anorg. Chem.*, 1929, 179, 345; for $\text{Na}_3\text{Au}(\text{SO}_3)_4 \cdot 5\text{H}_2\text{O}$, see Mingoia, *Gazzetta*, 1927, 57, 820.

³ *Canadian Patents*, 263180 (1924); 259884 (1925).

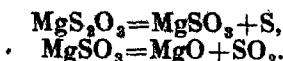
⁴ *German Patent*, 440380 (1925); *U.S. Patent*, 1638492 (1927). See also Scheneffeld, Vilbrandt and Withion, *Chem. and Met. Eng.*, 1921, 25, 953.

⁵ Picon, *Compt. rend.*, 1924, 178, 1548.

⁶ Rohrig, *J. prakt. Chem.*, 1888, 37, 225; Friend and Pounder, *J. Chem. Soc.*, 1928, p. 2245.

⁷ Foerster and Kubel, *Zeitsch. anorg. Chem.*, 1924, 139, 261. For various physical properties of the alkali sulphites and hydrogen sulphites, see Lewis and Rivett, *Trans. Chem. Soc.*, 1924, 125, 1156, 1162; Foerster, Brosche and Norberg-Schulz, *Zeitsch. physikal. Chem.*, 1924, 110, 435; Sabalitschka and Kubisch, *Arch. Pharm.*, 1924, 262, 105; Schüler and Wilhelm, *Zeitsch. angew. Chem.*, 1919, 32, 198.

At higher temperatures the following also occurs :



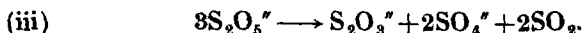
The decomposition of the alkali pyrosulphites under the influence of heat follows a very complicated course.¹ At 150° C. the potassium salt yields trithionate and sulphate, the ionic reaction being :



above 200° C. sulphur dioxide is liberated, and if the partial pressure of the sulphur dioxide (from (iii)) is kept low, the reaction



proceeds from left to right. The main reaction at 250° C., however, produces thiosulphate, thus :



A number of side reactions also occur, depending largely on concentration and temperature ; the thiosulphate gradually disappears and the final state may be represented :



The sodium salt behaves somewhat similarly, but the main reaction at 150° C. is that indicated in equation (ii).

The sulphites, both normal and acid, are easily oxidised, and in solution readily undergo atmospheric oxidation with the formation of sulphates. The oxidation proceeds more readily in neutral than in acid solution,² and is accelerated by warming. The change in SO_2 -content of a solution of potassium metabisulphite (0.1 per cent.) kept in a stoppered bottle, observed by titration at intervals of aliquot portions with standard iodine solution, has been observed to be as follows :³

Time interval (hours) .	0	24	48	72	96	144
Relative SO_2 -content .	100	98.2	94.6	93.5	92.2	91.3.

The oxidation can be considerably checked by the addition of certain organic compounds, such as sucrose,⁴ alcohols,⁵ quinol,⁶ and some organic acids. On the other hand it is accelerated by dextrose and certain other sugars,⁷ and also by the presence of Cu^{++} or Fe^{+++} ions in solutions of P_H value 4 to 12.⁸

¹ Foerster and Hamprecht, *Zeitsch. anorg. Chem.*, 1926, 158, 277.

² Mason and Walsh, *Analyst*, 1928, 53, 142. See also Sabalitschka and Kubisch, *Arch. Pharm.*, 1924, 262, 105.

³ Phillips, *Analyst*, 1928, 53, 150.

⁴ Maass and Maass, *J. Amer. Chem. Soc.*, 1928, 50, 1352.

⁵ Bigelow, *Zeitsch. physikal. Chem.*, 1898, 26, 493; Alyea and Bäckström, *J. Amer. Chem. Soc.*, 1929, 51, 90.

⁶ Lumière and Seyewetz, *Bull. Soc. chim.*, 1905, [iii.], 33, 444.

⁷ Hägglund, *Ber.*, 1929, 62, [B], 84, 437; Marusawa, Naito and Uchida, *Mem. Ryojun Coll. Eng.*, 1929, 1, 351.

⁸ Reinders and Vles, *Rec. Trav. chim.*, 1925, 44, 249. For changes occurring in solutions of various hydrogen sulphites in the presence of selenium as catalyst, see Sandonnini, *Atti R. Accad. Lincei*, 1923, [v.], 32, ii., 84.

Aqueous solutions of normal alkali sulphites are oxidised to dithionate by heating with lead dioxide,¹ the latter being reduced to red lead. Manganese dioxide does not react in this way.

Analogous to the action of oxygen is that of sulphur, which slowly converts a sulphite in hot aqueous solution into the corresponding thio-sulphate, some trithionate being formed simultaneously.² The reaction goes to completion with excess of sulphur, and is accelerated by the presence of sodium sulphide.

Crystalline *hydrazine derivatives* of certain sulphites, for example of zinc, cadmium, manganese, cobalt and nickel sulphites, have been prepared.³ When aqueous manganous sulphite containing excess of sulphurous acid is neutralised with hydrazine hydrate, a white crystalline compound, $\text{MnSO}_3 \cdot \text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_3$, is formed. A solution of cobalt hydrogen sulphite similarly treated yields a red compound of composition $5\text{CoSO}_3 \cdot 9\text{N}_2\text{H}_4 \cdot 6\text{H}_2\text{O}$, but if the hydrogen sulphite is added to an excess of concentrated hydrazine hydrate solution, a buff-coloured compound, $\text{CoSO}_3 \cdot 2\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, results. A suspension of the latter salt treated with sulphur dioxide gives two red sulphites, $\text{CoSO}_3 \cdot 2\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{CoSO}_3 \cdot \text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_3 \cdot 0.5\text{H}_2\text{O}$. The other (red) compound similarly treated yields a brown substance, $2\text{CoSO}_3 \cdot \text{N}_2\text{H}_4 \cdot 3\text{H}_2\text{O}$. Similar products from sulphites of the other metals mentioned may be obtained.

By the action of alkali hydrogen sulphites on alkali nitrites, compounds are obtained the structure of which may be derived from that of ortho-nitrous acid, $\text{N}(\text{OH})_3$, by substituting the sulphonic acid group, $-\text{SO}_2\text{OH}$, for one or more hydroxyl groups.

The acid sulphites possess the property of forming crystalline *additive compounds with aldehydes and ketones*.⁴ Sodium hydrogen sulphite is therefore largely used for the purification of compounds of these classes; the sulphite adds on at the carbonyl group, $>\text{C}:\text{O}$, forming the group-

ing $\text{>C} \begin{matrix} \text{OH} \\ \diagup \\ \text{O} \cdot \text{SO}_2\text{Na} \end{matrix}$, and the original organic substance can be liberated

by suitable treatment with acid or alkali.

Calcium bisulphite is largely used in the manufacture of "sulphite pulp," from which paper and viscose silk (see p. 264) may be produced. Wood chips or shavings are boiled with the bisulphite under pressure and so yield cellulose, which at the same time is bleached. The bisulphites of magnesium and the alkali metals are also sometimes used.

It is of interest that there is a frequent occurrence of isomorphism between the sulphites and the corresponding carbonates; this would appear, at first sight, to indicate quadrivalency of sulphur in the sulphites, but the evidence is untrustworthy and insufficient (see later).⁵

Constitution of Sulphurous Acid.—In deciding the constitution of sulphurous acid, choice has to be made between the two alternatives

¹ Hae, *Coll. Czech. Chem. Comm.*, 1929, 1, 259.

² Hargreaves and Dunningham, *J. Soc. Chem. Ind.*, 1923, 42, 147 T; Watson and Rajagopalan, *J. Indian Inst. Sci.*, 1925, 8, A, 275.

³ Rây and Goswami, *Zeitsch. anorg. Chem.*, 1928, 168, 329.

⁴ For the action of sulphites on other types of organic compounds, see Bucherer and Barsch, *J. prakt. Chem.*, 1925, [u.], 111, 313; Bucherer and Hoffmann, *ibid.*, 1929, [ii.], 121, 113; Hägglund and Ringbom, *Zeitsch. anorg. Chem.*, 1926, 150, 231.

⁵ The metallic sulphites are dealt with individually in other volumes of this series, under the various metals.

$\begin{array}{c} \text{O} \\ \diagup \\ \text{S} \\ \diagdown \\ \text{O} \end{array} \begin{array}{c} \text{OH} \\ \diagup \\ \text{H} \end{array}$ and $\text{O}=\text{S} \begin{array}{c} \text{OH} \\ \diagup \\ \text{OH} \end{array}$, which may respectively be designated as the unsymmetrical structure and the symmetrical structure.¹ It may be stated at once that no absolute decision is at present possible with respect to the inorganic salts of sulphurous acid and the aqueous acid itself, although clear evidence is obtained with the organic sulphites.

When an alkali sulphite is allowed to react with the bromide or iodide of an organic radical, for example with ethyl iodide, the resulting compound, ethylsulphonic acid, undoubtedly possesses the unsym-

metrical structure, $\begin{array}{c} \text{O} \\ \diagup \\ \text{S} \\ \diagdown \\ \text{O} \end{array} \begin{array}{c} \text{OH} \\ \diagup \\ \text{C}_2\text{H}_5 \end{array}$, because not only does the correspond-

ing diethyl compound $\begin{array}{c} \text{O} \\ \diagup \\ \text{S} \\ \diagdown \\ \text{O} \end{array} \begin{array}{c} \text{OC}_2\text{H}_5 \\ \diagup \\ \text{C}_2\text{H}_5 \end{array}$ (ethyl ethylsulphonate) merely

undergo decomposition to the stage of the potassium salt $\text{C}_2\text{H}_5\text{SO}_2\text{OK}$ when heated with aqueous potassium hydroxide solution, but also the parent ethylsulphonic acid can be obtained by the oxidation of ethyl hydrogen sulphide, $\text{C}_2\text{H}_5\text{S.H}$, in which the ethyl radical is certainly attached directly to sulphur.²

On the other hand, thionyl chloride reacts with ethyl alcohol to produce a compound of the symmetrical structure $\text{O}=\text{S} \begin{array}{c} \text{O.C}_2\text{H}_5 \\ \diagup \\ \text{O.C}_2\text{H}_5 \end{array}$.

This diethyl sulphite is a colourless liquid of b.pt. 161°C. , and is quite distinct from the foregoing isomeric ethyl ethylsulphonate (which boils at 207°C.), being decomposed by aqueous alkali with formation of alkali sulphite and ethyl alcohol² and reacting with organo-magnesium

compounds with the formation of a sulphoxide, $\begin{array}{c} \text{R} \\ \diagup \\ \text{S}=\text{O} \\ \diagdown \\ \text{R} \end{array}$, where R represents the organic radical.³

Organic compounds are therefore obtainable representative of both the symmetrical and the unsymmetrical structures. Only one series of inorganic salts is known, however, and the task of definitely assigning to them one of the structures is a matter of great difficulty, because the purely inorganic evidence is conflicting.⁴

Whilst the formation of thionyl chloride by the action of phosphorus pentachloride on an alkali sulphite favours a symmetrical structure for the latter, the interaction of an alkali sulphite with ethyl iodide, as mentioned already, is directly opposed to this evidence, as also is the production of sodium sulphite on reducing sodium dithionate with sodium.⁵ The remaining inorganic evidence is little more satisfactory.

What appeared to be final evidence was once brought forward in

¹ Strecker, *Annalen*, 1868, 148, 90; Michaelis and Wagner, *Ber.*, 1874, 7, 1073.

² Michaelis and Wagner, *loc. cit.*; Michaelis, *Annalen*, 1873, 170, 31; Blomstrand, *Ber.*, 1870, 3, 957; Barbaglia, *ibid.*, 1872, 5, 270; Dixon, *Phil. Mag.*, 1886, [v.], 21, 127.

³ Strecker, *Ber.*, 1910, 43, 1131.

⁴ See Divers, *Trans. Chem. Soc.*, 1885, 47, 205; Divers and Shimidzu, *ibid.*, 1886, 49, 577; Spring, *Ber.*, 1874, 7, 116; Rosenheim and others, *ibid.*, 1898, 31, 405; 1904, 37, 2152; 1905, 38, 1298; Stokes, *Trans. Chem. Soc.*, 1869, 22, 174; Baubigny, *Compt. rend.*, 1910, 150, 973.

⁵ Baubigny, *loc. cit.*

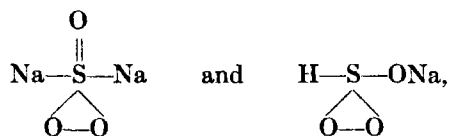
the description of two isomeric salts obtained by the neutralisation of sodium hydrogen sulphite with potassium carbonate solution and of potassium hydrogen sulphite with sodium carbonate solution.¹ These two salts dissolved in water to give identical solutions, in accordance with the theory of electrolytic dissociation, and their structures were

assumed to be $\text{Na}-\overset{\text{O}}{\underset{\text{O}}{\parallel}}\text{S}-\text{O}-\text{K}$ and $\text{K}-\overset{\text{O}}{\underset{\text{O}}{\parallel}}\text{S}-\text{O}-\text{Na}$, respectively, the

former yielding crystals with two molecules of water of crystallisation, the latter with one. Subsequent workers, however, have been unable to confirm these observations.²

No final or absolute decision is therefore yet possible. By analogy with other cases of a similar type amongst organic compounds, the possibility of a "dynamic isomerism" must not be left out of consideration. It is quite possible that in sulphurous acid solution, molecules of the symmetrical and the unsymmetrical constitution may be present, side by side, in equilibrium with one another, and that even in solutions of the salts a similar condition of equilibrium may exist. Indeed, the distinctly contradictory nature of some of the chemical evidence favours this view.

Raschig³ suggests that the normal and acid sulphites may be respectively formulated as



these structures indicating the tautomeric forms in which the acid may exist. The unsymmetrical constitution of bisulphites is in accordance with the formation of (a) amidosulphonic acid by the action of hydroxylamine hydrochloride on sodium hydrogen sulphite in the presence of excess of sulphurous acid, and (b) hydrosulphurous acid by the reduction of hydrogen sulphites. The fact that normal sulphites do not react with nitrites may be explained by "steric hindrance," due to the central position of the sulphur atom.

Sulphur Trioxide, SO_3 .

Historical.—The first mention of sulphur trioxide is by Basil Valentine at the end of the fifteenth century. The method of formation by heating ferrous sulphate was first described in 1675 by Lemery, whilst the preparation by heating fuming sulphuric acid was discovered a century later by Bernhardt. Scheele and Guyton de Morveau first recognised the compound as *sulphuric anhydride*.

¹ Rohrig, *J. prakt. Chem.*, 1888, [2], 37, 250; Schwicker, *Ber.*, 1889, 22, 1728; Barth, *Zeitsch. physikal. Chem.*, 1892, 9, 176.

² Fraps, *Amer. Chem. J.*, 1900, 23, 202; Godby, *Proc. Chem. Soc.*, 1907, 23, 241; Arbusoff, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 447.

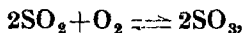
³ Raschig, *Schwefel- und Stickstoff-studien*, 1924, pp. 1, 225, 242; *Chem. Zentr.*, 1924, ii., 16, 1069, 1093.

Formation and Preparation.—(1) Sulphur trioxide is formed to a small extent together with sulphur dioxide when sulphur¹ or compounds of sulphur² are burned in oxygen or air (see p. 108). In an oxygen bomb, in the presence of a compound which on combustion yields water vapour and oxides of nitrogen, for example ammonium nitrate, the combustion goes completely to sulphur trioxide (see p. 45).³

(2) (a) Sulphur dioxide, when exposed to strong illumination, undergoes partial and reversible conversion into sulphur and sulphur trioxide (p. 114).

(b) Sulphur dioxide is easily converted into the trioxide by the action of oxygen and gentle heat. Above 450° C. there is a tendency towards the formation of an equilibrium mixture of sulphur dioxide and trioxide with oxygen, but below this temperature the amount of dioxide in the equilibrium mixture is almost inappreciable. It is inadvisable, therefore, to allow the reaction to occur at too high a temperature, but, at the same time, the temperature must not be too low, otherwise the rate of change will be very slow.

The change has been submitted to careful physico-chemical examination⁴ and is found to accord with the usual method of expression,



in agreement with which are the facts that the reaction is termolecular and that increase in pressure greatly favours the formation of trioxide.

The presence of traces of moisture exerts a very considerable favourable effect on the rate of combination of the gases; reaction after drying with phosphorus pentoxide is relatively sluggish.⁵

Many solid substances are remarkably active in accelerating the change; especial mention may be made of finely divided platinum⁶ in this respect. In the presence of platinum black at a temperature of 432° C., 96.8 per cent. of the dioxide may be converted into the trioxide.⁷ Sugar charcoal and the oxides of iron, copper, vanadium and arsenic⁸ are amongst other substances which possess catalytic power over the reaction, and although they are weaker catalysts than platinum, the final proportions of dioxide and trioxide in the equilibrium mixture are but little affected by the nature of the catalyst used.⁹ The present

¹ Hempel, *Ber.*, 1890, 22, 1455; Cornog, Dargan and Bender, *J. Amer. Chem. Soc.*, 1926, 48, 2757.

² Scheurer-Kestner, *Compt. rend.*, 1875, 80, 1230; 1884, 99, 917; Lunge and Salathe, *Ber.*, 1877, 10, 1824.

³ Bradley, Corbin and Floyd, *Ind. Eng. Chem.*, 1926, 18, 583; Kohout, *ibid.*, 1927, 19, 1065.

⁴ Buff and Hofmann, *Annalen*, 1860, 113, 129; Wilde, *Ber.*, 1874, 7, 356; Knietzsch, *ibid.*, 1901, 34, 4069; Winkler, *Dingl. poly. J.*, 1875, 218, 128; Hess, *Ann. Phys. Chem.*, 1842, [ii.], 56, 471; Thomsen, *ibid.*, 1873, [ii.], 150, 32; Deville, *Bull. Soc. chim.*, 1865, [ii.], 3, 366; Bodländer and Koppen, *Zeitsch. Elektrochem.*, 1903, 9, 559; Lucas, *ibid.*, 1905, 11, 457; Bodenstein, *ibid.*, 1903, 9, 696; Bodenstein and Pohl, *ibid.*, 1905, 11, 373; Bodenstein and Fink, *Zeitsch. physikal. Chem.*, 1907, 60, 1, 46; Bodenstein, *ibid.*, 1912, 80, 148; Wöhler, Foss and Plüddemann, *Ber.*, 1906, 39, 3538; Findlay, *Zeitsch. Elektrochem.*, 1906, 12, 129; Coehn and Becker, *Zeitsch. physikal. Chem.*, 1910, 70, 88; Wieland, *Ber.*, 1912, 45, 685.

⁵ Berl, *Zeitsch. anorg. Chem.*, 1905, 44, 287.

⁶ Phillips, *British Patent*, 6096 (1831); Magnus, *Ann. Phys. Chem.*, 1832, [ii.], 24, 610.

⁷ Wenger and Ufer, *Ann. Chim. anal.*, 1918, 23, 97.

⁸ Mahla, *Annalen*, 1852, 81, 255; Russell and Smith, *Proc. Chem. Soc.*, 1900, 16, 41; Doroshevski and Pavlov, *J. Russ. Phys. Chem. Soc.*, 1917, 49, 169.

⁹ Küster, *Zeitsch. anorg. Chem.*, 1904, 42, 453.

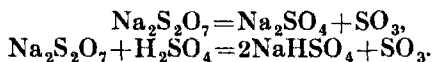
commercial process for the manufacture of sulphur trioxide is based on the use of such catalysts (see the "Contact Process" for the manufacture of sulphuric acid, p. 159).

(c) When a mixture of sulphur dioxide and oxygen is subjected to the silent electric discharge, more or less complete conversion into sulphur trioxide occurs, the amount of conversion depending upon the composition and pressure of the gaseous mixture.¹ If oxygen is activated alone by the discharge it readily unites with sulphur dioxide after removal, but sulphur dioxide is not itself activated by the discharge.²

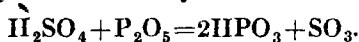
(3) (a) Fuming sulphuric acid,³ when carefully distilled into a well-cooled receiver, gives a crystalline deposit of sulphur trioxide as the first fraction; ordinary sulphuric acid remains in the retort:



(b) The pyrosulphates resemble their parent acid (see (3) (a)) in yielding sulphur trioxide when heated;⁴ a similar result is obtained on heating with sulphuric acid:⁵

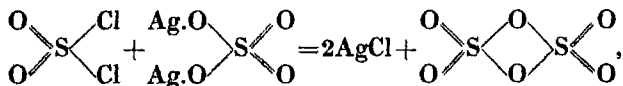


(4) (a) The elements of water can be removed from sulphuric acid by treating with an excess of phosphorus pentoxide,⁶ when the resulting sulphur trioxide may be removed by distillation:



(b) Many metal sulphates derived from the more feebly basic metals when strongly heated in an anhydrous condition are converted into oxide, with loss of sulphur trioxide.⁷ Ferric sulphate is one of the best known examples. On account of the high temperature necessary there is a tendency, however, for the sulphur trioxide to undergo partial decomposition into dioxide and oxygen, and a similar tendency is observable with the pyrosulphates (see (3) (b)). With both classes of salts reduction of pressure allows evolution of the trioxide to occur at a lower temperature and so renders the result more satisfactory.

(5) Especially interesting from the evidence which it supplies as to the possibility of a bimolecular structure for sulphur trioxide is the formation of this substance when sulphuryl chloride and silver sulphate are heated together.⁸ This reaction would be expected to follow the course



¹ Poliakov, *Sci. Mag. Chem. Cath. Katerinoslav*, 1926, p. 207.

² For the influence of α -particles on the reaction, see Maisan, *Ann. Soc. Sci. Bruxelles*, 1927, 47, B, i., 172.

³ Osann, *Dingl. poly. J.*, 1859, 151, 158; Schultz-Sellack, *Ber.*, 1871, 4, 110; Vogel and Partington, *Trans. Chem. Soc.*, 1925, 127, 1514.

⁴ Prelier, *Pharm. Centr.*, 1848, 19, 304; Wolters, *Dingl. poly. J.*, 1878, 230, 451; *Ber.*, 1878, 11, 1946.

⁵ Wolters, *Ber.*, 1881, 14, 122.

⁶ Barreswil, *Compt. rend.*, 1847, 25, 30; Evans, *Trans. Pharm. J.*, 1849, 8, 127; Nobel and Fehrenbach, *Ber.*, 1885, 18, 201.

⁷ Schubert, *Ber.*, 1890, 23, 515; Hill, *Chem. News*, 1895, 72, 75; Keppeler and d'Ans, *Zeit. physikal. Chem.*, 1908, 62, 89; Wöhler, Pfüddemann and Wöhler, *Ber.*, 1908, 41, 703.

⁸ Odling and Abel, *Trans. Chem. Soc.*, 1855, 7, 2; Divers, *ibid.*, 1886, 49, 584.

and, as will be seen later, sulphur trioxide can exist in a bimolecular condition (see p. 144).

The trioxide, produced by any of the preceding methods, can be purified by repeated distillation, followed by treatment with phosphorus pentoxide at 90° to 100° C., being finally separated from the pentoxide by distillation or decantation.¹

Physical Properties.—It has long been recognised that sulphur trioxide is capable of existence in more than one form,² but the exact nature of the polymorphs has been difficult to define owing to gross irregularities observable in the physical properties of different specimens and even of individual specimens after lapse of time.

Two solid forms, distinguished as α - and β -modifications, were described by Marignac³ and others⁴ and are now generally recognised. The α - or "ice" form is that corresponding with ordinary molten sulphur trioxide; it consists of colourless prismatic crystals which melt at 16·8° C. to a fairly mobile liquid, less viscous than sulphuric acid. The pure liquid is colourless, but the presence of organic matter causes a brown coloration. The density of the liquid has been found to be as follows :

Temperature, °C.	Density.	Observer.	Temperature, °C.	Density.	Observer.
11	1·944	Schenck ⁵	40	1·8335	Berthoud ⁷
16	1·940	Weber ⁶	50	1·7812	"
20	1·9255	Berthoud ⁷	60·4	1·718	Schenck ⁵
25	1·9040	"	80·3	1·617	"
30	1·8819	"	100·0	1·529	"

The liquid has a coefficient of expansion of 0·002005⁸ for the temperature range 15° to 20° C., a refractive index, $n_D^{20} = 1·40965$,⁹ and boils at 44·8° C. under 760 mm. pressure.¹⁰ When kept at a temperature below 25° C. for a considerable period, it undergoes gradual conversion into the more stable β -form, which slowly separates; for this reason the earlier boiling-point data in the literature show considerable variation. Experiments with solutions of sulphuric acid, sulphonal and trional in the liquid indicate a value of 18·5 for the ebullioscopic constant.¹¹

β -Sulphur trioxide, the more stable solid form, usually consists of long fibrous needles, and is designated the "asbestos" form. When heated above 50° C. it vaporises without melting, but in a sealed tube the crystals melt over the range 50° to 80° C.

¹ Weber, *Ann. Phys. Chem.*, 1876, [N.], 159, 315; *Ber.*, 1886, 19, 3187.

² Marignac, *Arch. Sci. phys. nat.*, 1853, 22, 225; 1875, 52, 236.

³ Marignac, *loc. cit.*

⁴ Schultz-Sellack, *Ber.*, 1870, 3, 215; *Bull. Soc. chim.*, 1870, 14, 154; Oddo, *Gazzetta*, 1901, 31, ii, 158; Schenck, *Annalen*, 1901, 316, 1.

⁵ Schenck *loc. cit.*

⁶ Weber, *Pogg. Annalen*, 1876, 159, 313.

⁷ Berthoud, *Helv. Chim. Acta*, 1922, 5, 513.

⁸ Lichty, *J. Amer. Chem. Soc.*, 1912, 34, 1440.

⁹ Nisini, *Ber.*, 1882, 15, 2885; *Gazzetta*, 1927, 57, 687.

¹⁰ Smits and Schoenmaker, *J. Chem. Soc.*, 1926, p. 1108.

¹¹ Beckmann, *Zeitsch. anorg. Chem.*, 1912, 77, 90.

As would be expected from its increasing dissociation at higher temperatures, sulphur trioxide is formed from sulphur dioxide and oxygen with evolution of heat, the amount being 32.1 Calories per gram-molecule formed, whilst the heat of formation of the liquid trioxide from its elements is 103.2 Calories per gram-molecule.¹ The latent heat of vaporisation per gram-molecule of liquid sulphur trioxide is 10.3 Calories.²

In accordance with its nature as the more stable form, β -sulphur trioxide is found to give lower vapour pressures than the α -modification, whilst its heat of formation with respect to its elements, namely 111.6 Calories, is greater.

The existence of two polymorphs was questioned by Weber,³ who maintained that the β -form was a hydrate of sulphur trioxide, and this also was the conclusion arrived at by Berthoud,⁴ after determinations of the melting-points of the two forms, and of the vapour pressures of liquid sulphur trioxide. The latter investigator, however, described it as a hydrate unique in its remarkably small water content—estimated at less than 1 molecule per million molecules of trioxide.

Again, Le Blanc and Rühle,⁵ in order to interpret the results of a large number of observations of the vapour pressures of solid and liquid sulphur trioxide, using specimens prepared by different methods, and also from melting-point determinations, found it necessary to postulate four different modifications, namely "A" (m.pt. 95° to 100° C.), "B" (m.pt. 31° C.), "C" (m.pt. 16.8° C.), "D" (m.pt. lower than 16.8° C.). "C" was obviously the α -form.

Oddo expressed the view that the α -form—liquid sulphur trioxide—could be represented by the simple formula SO_3 , whilst the more stable β -form—ordinary fibrous or "asbestos" sulphur trioxide—was to be regarded as a dimeride $(\text{SO}_3)_2$. This view followed from a series of determinations of freezing-point depressions and vapour density measurements.⁶ In the former experiments irregular values were obtained when liquid sulphur trioxide was used as solute, owing to the formation of solid solutions. The results, however, using phosphorus oxychloride as solvent, agreed with a molecular weight corresponding to the simple formula. With sulphuryl chloride and ethyl chloroacetate as solvents the values for the fibrous form corresponded to a theoretical molecular weight of 160. Vapour density determinations for liquid and fibrous sulphur trioxide gave mean values of 82.68 and 83.77 for the respective molecular weights. Thus a small degree of association in the vapour state is indicated, though this can scarcely be seen in the following data obtained by earlier investigators :

¹ Thomsen and Burke, *Thermochemistry*, p. 210 (Longmans, 1908); Berthelot, *Compt. rend.*, 1877, 84, 676; 1880, 90, 1449; Bodländer and Koppen, *Zetsch. Elektrochem.*, 1903, 9, 787; Bodenstein and Pohl, *ibid.*, 1905, 11, 373.

² Berthoud (*loc. cit.*) calculated from vapour tension values; Berthollet (*Compt. rend.*, 1880, 90, 1510) gives 11.8 Calories.

³ Weber, *loc. cit.*; *Ber.*, 1886, 19, 3187. See also Rebs, *ibid.*, 1888, 21, 596.

⁴ Berthoud, *loc. cit.*

⁵ Le Blanc and Rühle, *Ber. Mat. phys. Klass. Sachs. Akad. Wiss.*, 1922, 74, 106.

⁶ Oddo, *Gazzetta*, 1901, 31, [ii.], 158; 1927, 57, 29; Oddo and Casalino, *ibid.*, 57, 47, 60, 75; Lichty (*loc. cit.*), however, found the same molecular weight for both the α - and β -forms.

Pressure, mm. Hg.	Temperature, ° C.	Density (Hydrogen = 1).	Observer.
22.1	22.8	40.0	Perman. ¹
40.5	22.7	39.2	"
56.7	22.1	40.9	"
760	46	39.4-39.7	Schultz-Sellack. ²

The behaviour of the asbestos-like β -form is more complex, however, than can be accounted for by regarding it as a simple dimeride, and several chemists have expressed the belief that it contains two distinct constituents, one unimolecular and the other bimolecular; the former is described as a fusible crystalline solid, melting at about 80°C. , and the latter as an infusible substance.³

What appears to be a probable solution to the problem has been put forward by Smits and Schoenmaker⁴ after an investigation of the changes in vapour pressure and the corresponding changes in the melting temperature of the intensively dried and purified substance. Two "asbestos" forms were separated by distillation under reduced pressure, a high-melting form, m.pt. 62.2°C. , and a low-melting form, m.pt. 32.5°C. The third form corresponded to α -sulphur trioxide, or the "ice" form, of m.pt. 16.8°C. ⁵ It was found that with each form the vapour pressure diminishes continually. Thus, after the "ice" form had stood for fifty-six hours at 18°C. the vapour pressure at 0°C. diminished by 71.4 mm. of mercury, and on repeated distillation it fell continuously to 22 mm., the initial value having been 207.8 mm. During this fall, the initial melting-point first rose and then fell. Similarly with the high-melting "asbestos" form, the fall of vapour pressure after distillation was very marked. At 50°C. a decrease from 591 to 37 mm. of mercury was noted, but on keeping the substance at this temperature the value slowly increased, after nineteen hours being 214.5 mm., and recovering its original value after 159 days, further increasing to 626.2 mm. after 255 days. It was found that the sample both before and after these changes gave identical X-ray photographs. The effect of the X-rays was to give a rapid increase in the value of the vapour pressure. The low-melting "asbestos" form, which was obtained as clusters of fine needles, did not lend itself to intensive drying, since it readily passed to the high-melting form; but samples which were not intensively dried showed behaviour similar to the foregoing. The high-melting form, which is the stable form of sulphur trioxide, was obtained by cooling the "ice" form in liquid air or distilling repeatedly at 18° to -80°C. Above 18°C. the "ice" form is a clear liquid.

In order to explain the foregoing behaviour, Smits and Schoenmaker assume that sulphur trioxide consists of a mixture of two different kinds of molecules which not only change one into the other, but combine to

¹ Perman, *Proc. Roy. Soc.*, 1890, 48, 57.

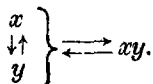
² Schultz-Sellack, *Ber.*, 1870, 3, 215.

³ Schenck, *Annalen*, 1901, 316, 1; Oddo, *loc. cit.*; Giran, *Compt. rend.*, 1913, 157, 221; Lichty, *loc. cit.*

⁴ Smits, *Chem. Weekblad*, 1924, 21, 594; Smits and Schoenmaker, *Trans. Chem. Soc.*, 1924, 125, 2554; 1926, pp. 1108, 1603.

⁵ Cf. the "A," "B" and "C" forms of Le Blanc and Röhle.

give a dissociable compound, the reactions leading to the attainment of an inner equilibrium which may be represented as



The various modifications of sulphur trioxide will therefore act as mixtures of these three constituents. In an ordinary preparation the condition of equilibrium is more or less rapidly attained, but in an intensively dried material the velocity of such inner transformation is considerably retarded.¹ On realising this condition, as already shown, both the solid and liquid states behave as mixtures. Exposure to X-rays accelerates the attainment of the inner equilibrium.

The critical data for sulphur trioxide have been found to be as follows:² Critical pressure, 83.8 atmospheres; critical temperature, 218.3° C.; critical density, 0.633.

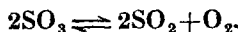
Chemical Properties.—Both the α - and β -forms of sulphur trioxide exhibit as a rule the same chemical behaviour, although the β -variety is less active.

At the ordinary temperature sulphur trioxide forms dense fumes in moist air, caused by the formation of sulphuric acid. The anhydrous substance possesses no acidic properties, but combines violently with water, producing pyrosulphuric and then sulphuric acid, the heat evolution with a large excess of water amounting to 40.3 Calories per gram-molecule of SO_3 .³ The heats of dilution (H) for one gram-molecule of SO_3 with n molecules of H_2O are as follows:⁴

$n = 1$	2	3	5	1600
$H = 21.3$	28.04	31.31	34.14	40.34 Cals.

Its affinity for water causes sulphur trioxide to carbonise many organic substances.

From examination of the vapour density it is known that the trioxide undergoes no appreciable dissociation below 430° C., but at higher temperatures the percentage of dissociated molecules increases, until at near 1000° C. the vapour consists entirely of sulphur dioxide and oxygen.⁵ The catalysts which accelerate the formation of sulphur trioxide also facilitate its dissociation:



The trioxide possesses marked oxidising properties, in the exercise of which it is generally reduced to the dioxide. Yellow phosphorus soon inflames in the vapour at the ordinary temperature, some of the trioxide being reduced even to sulphur.⁶ Phosphine is oxidised by solid sulphur trioxide with formation of phosphorus.⁷ Phosphorus trichloride

¹ See H. B. and M. Baker, *Trans. Chem. Soc.*, 1912, 101, 2339.

² Berthoud, *J. Chim. phys.*, 1923, 20, 77; *Helv. Chim. Acta*, 1922, 5, 513. Other physical properties of sulphur trioxide are also given.

³ Porter, *Trans. Faraday Soc.*, 1918, 13, 373. See also Thomsen, *Ber.*, 1873, 6, 713; Berthelot, *Compt. rend.*, 1873, 77, 27; 1880, 90, 1511.

⁴ Porter, *loc. cit.*

⁵ Knietach, *Ber.*, 1901, 34, 4069; Bodenstein and Kranendieck, *Zeitsch. physikal. Chem.*, 1912, 80, 148.

⁶ Vogel, *J. Chem. Phys.* (*Schweigger*), 1812, 4, 121.

⁷ Rose, *Ann. Phys. Chem.*, 1834, [ii.], 24, 140; Aimé, *J. prakt. Chem.*, 1835, 6, 79, 1872.

is converted into the oxychloride. Hydrogen bromide and iodide yield bromine and iodine, respectively,¹ whereas hydrogen chloride, as already described (p. 98), gives rise to chlorosulphonic acid. At a red heat the metals iron, magnesium and zinc are converted into a mixture of the corresponding metallic sulphide and oxide,² whilst mercury reacts at a much lower temperature, with the formation of sulphate and sulphur dioxide.³ Many metal sulphides, for example those of the alkalis, and of lead and antimony, are oxidised to sulphates, with simultaneous production of sulphur dioxide or sulphur.⁴ Sulphur trioxide frequently also exerts oxidising power towards organic substances, as for instance towards carbon disulphide,⁵ which at higher temperatures gives carbon oxysulphide (see below), but the action with organic compounds is more commonly one of sulphonation.

Reduction of sulphur trioxide by hydrazine gives rise to sulphur sesquioxide,⁶ possibly by primary formation of sulphur, which combines with unaltered trioxide (see p. 224).

Under the influence of the silent electric discharge sulphur trioxide combines with oxygen to form the so-called heptoxide or persulphuric anhydride, S_2O_7 ,⁷ (cf. p. 180). At the ordinary temperature it forms an unstable blue sesquioxide, S_2O_3 , with sulphur, whilst with selenium and tellurium it forms the analogous compounds $SeSO_3$ and $TeSO_3$.⁸ Iodine combines with a termolecular proportion of sulphur trioxide, giving a product $I(SO_3)_3$, from which the trioxide can be removed in several stages.⁹

With many acid anhydrides sulphur trioxide condenses to form "mixed anhydrides";⁹ thus, nitric anhydride gives $N_2O_5 \cdot 4SO_3$, possibly of the constitution $NO_2 \cdot O \cdot SO_2 \cdot O \cdot SO_2 \cdot O \cdot SO_2 \cdot O \cdot NO_2$; nitrogen trioxide dissolved in carbon tetrachloride yields $2N_2O_3 \cdot 5SO_3$; at $120^\circ C.$ boric anhydride gives $B_2O_3 \cdot SO_3$, whilst at $230^\circ C.$ the product is $B_2O_3 \cdot 2SO_3$; chromic anhydride at $70^\circ C.$ yields $CrO_3 \cdot SO_3$; phosphoric oxide, arsenious oxide and selenium dioxide give the compounds $P_4O_{10} \cdot 6SO_3$, $As_4O_6 \cdot 2SO_3$ and $SeO_2 \cdot SO_3$, respectively. In the cold, carbon disulphide combines with sulphur trioxide forming a crystalline additive compound,¹⁰ in which the former constituent, as a thio-anhydride, possibly functions in a similar manner to the ordinary anhydrides in the compounds just described; when warmed, this additive compound decomposes with formation of carbon oxysulphide, as already mentioned. Sulphur dioxide is absorbed by sulphur trioxide, giving a liquid containing up to approximately 70 per cent. of the former and probably representing an unstable compound.

Sulphur trioxide combines with sulphuric acid, producing pyro-

¹ Michaelis, *Zeitsch. Chem.*, 1871, [ii.], 7, 151; Armstrong, *J. prakt. Chem.*, 1870, [ii.], 1, 244; Clausnizer, *Ber.*, 1878, 11, 2012.

² d'Heureuse, *Annalen*, 1848, 68, 242; Brückner, *Monatsh.*, 1905, 26, 675.

³ Vogel, *loc. cit.*

⁴ Geuther, *Annalen*, 1859, 111, 177.

⁵ Armstrong, *Ber.*, 1869, 2, 712.

⁶ Ephraim and Piotrowski, *ibid.*, 1911, 44, 386.

⁷ Berthelot, *Compt. rend.*, 1878, 86, 20.

⁸ Weber, *J. prakt. Chem.*, 1882, [ii.], 25, 218; *Ber.*, 1887, 20, 87.

⁹ Picotet and Karl, *Compt. rend.*, 1907, 145, 238; *Bull. Soc. chim.*, 1908, [iv.], 3, 1114; Adie, *Chem. News*, 1889, 59, 58; *Trans. Chem. Soc.*, 1891, 59, 230; Weber, *Ann. Phys. Chem.*, 1864, [ii.], 123, 337; 1871, [ii.], 142, 602; *Ber.*, 1887, 20, 3, 86; 1886, 19, 3185; Stavenhagen, *Zeitsch. anorg. Chem.*, 1893, p. 283; Rose, *Ann. Phys. Chem.*, 1836, [ii.], 39, 175; Schultz-Sellack, *ibid.*, 1870, [ii.], 139, 480.

¹⁰ Armstrong, *loc. cit.*

sulphuric acid,¹ whilst the sulphates yield pyrosulphates. Perdisulphates also absorb the trioxide, giving the so-called "per-pyrosulphates"; thus potassium perdisulphate combines with a bimolecular proportion of the trioxide to form potassium per-pyrosulphate, $K_2S_4O_{14}$, probably $K_2S_2O_8 \cdot O_2 \cdot S_2O_6 \cdot K_2$.

It has already been recorded (p. 142) that hydrogen chloride and sulphur trioxide react to produce chlorosulphonic acid. The alkali chlorides, on the other hand, form chloropyrosulphonates, *e.g.* $ClSO_2 \cdot O \cdot SO_2 \cdot ONa$, which are crystalline solids, decomposed by water;² the alkali fluorides, however, yield the corresponding fluorosulphonates, such as $F \cdot SO_3Na$ ³ (see p. 86). Sodium nitrite produces a "nitrosotrisulphonate," $NO_2(SO_3)_3Na$.² Alkali chlorides may be converted to sulphates with evolution of chlorine by the action at 300° to 600° C. of a mixture of sulphur trioxide and air. No fusion occurs nor does the evolved gas contain any sulphur dioxide.⁴

Towards many chlorinating agents the α - and β -varieties behave differently.⁵ Thus with phosphorus pentachloride the α -form yields phosphorus oxychloride with some pyrosulphuryl chloride, $S_2O_5Cl_2$, and evolution of sulphur dioxide and chlorine; the β -form yields the two former products, but neither sulphur dioxide nor chlorine is evolved. Sulphur monochloride with the α -form yields the dichloride and sulphur dioxide; with the β -form no gas is evolved. With carbon tetrachloride, pyrosulphuryl and carbonyl chlorides are formed, the reaction being much more rapid with the α - than with the β -variety. The following has been suggested as the course taken by the latter reaction, which is shown by the velocity constant to be unimolecular:



Constitution.—As has been stated earlier, sulphur trioxide in the gaseous condition is unimolecular and is therefore correctly represented by the molecular formula SO_3 .

At one time, influenced largely by the fact that in sulphur tetrachloride sulphur attained its highest state of valency towards any univalent element, many chemists preferred to regard sulphur as never exceeding a quadrivalent condition, and therefore expressed the molecular

structure of sulphur trioxide by the formula $O=S \begin{smallmatrix} \diagup O \\ | \\ \diagdown O \end{smallmatrix}$.⁶ This argument

was destroyed by the discovery of sulphur hexafluoride, and to-day the molecular constitution $O=S \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$ for the unimolecular condition is

fairly generally accepted.⁷

For the bimolecular substance, which appears to be the essential constituent of the "asbestos" form or the β -trioxide (p. 139), the

¹ Schulze, *Ber.*, 1884, 17, 2705.

² Schultz-Sellack, *ibid.*, 1871, 4, 109; Traube, *ibid.*, 1913, 56, 2513; also Ditte, *Compt. rend.*, 1900, 131, 143.

³ Traube, *Ber.*, 1913, 46, 2525; Schultz-Sellack, *loc. cit.*

⁴ Zellstoff-fabrik Waldhof and Schmidt, *British Patent*, 249474 (1925).

⁵ Oddo and Soconzo, *Gazzetta*, 1927, 57, 83.

⁶ Schröder, *Ann. Phys. Chem.*, 1882, [iii.], 16, 660; Divers, *Trans. Chem. Soc.*, 1886, 49, 584.

⁷ Oddo, *Gazzetta*, 1901, 32, [ii.], 158.

molecular constitution



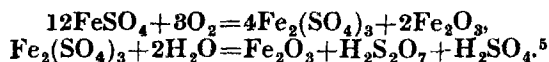
is probable,¹ the possibility of

such a structure being indicated by the method of formation (5) (p. 187), and supported by the differences in chemical behaviour, especially towards chlorinating agents as already indicated.² Moreover, that the change from the α - to the β -form involves polymerisation is suggested by the fact that the α -form can be stabilised for many months by the presence of certain negative catalysts, such as small amounts of sulphur, tellurium, carbon tetrachloride, or phosphorus oxychloride;³ this is analogous to the preservative action of such catalysts on an aldehyde. A specimen of asbestos-like sulphur trioxide, after being kept for twelve years, has been found by cryoscopic methods to have a molecular weight corresponding approximately with $(\text{SO}_3)_5$.⁴

Pyrosulphuric Acid, $\text{H}_2\text{S}_2\text{O}_7$.

Although the substance of the composition $\text{H}_2\text{S}_2\text{O}_7$ is capable of definite existence, the commercial products deviate from the composition expressed by the formula and contain variable quantities of sulphuric acid with pyrosulphuric acid or of pyrosulphuric acid with sulphur trioxide. For the purpose of including all varieties of impure pyrosulphuric acid, the somewhat vague terms "*oleum*," "*fuming sulphuric acid*" and "*Nordhausen sulphuric acid*" are advantageous.

Preparation.—(1) At one time fuming sulphuric acid was largely prepared by the dry distillation of basic ferric sulphate which had been obtained by submitting ferrous sulphate to atmospheric oxidation and subsequently dehydrating the oxidation product fairly completely:



The acid obtained will naturally vary in composition according to the extent of the previous dehydration.

In the fifteenth and sixteenth centuries the alchemists obtained sulphuric acid in this manner, frequently aiding the process by the addition of silica, and the process was worked on a commercial scale until the end of the nineteenth century. From the fact that much of the fuming acid was distributed from Nordhausen in Prussia, the name "*Nordhausen sulphuric acid*" originated, but little if any of the acid was manufactured in this town.⁶

(2) The present method of manufacture is to treat ordinary sulphuric acid with the necessary amount of sulphur trioxide,⁷ by which procedure any desired degree of concentration may be attained. The trioxide may be introduced in the liquid condition, but commercially it is simpler to pass the trioxide vapours from the contact chambers (p. 160) directly into sulphuric acid of 98 to 99 per cent. concentration. The latter is usually contained in bubbling vessels or circulated in towers. The vapours

¹ Oddo, *Gazzetta*, 1901, 32, [ii.], 158.

² Oddo and Sconzo, *loc. cit.*

³ Oddo and Sconzo, *loc. cit.*

⁴ Oddo, *Gazzetta*, 1927, 57, 29.

⁵ Keppeler and d'Ans, *Zeitsch. physikal. Chem.*, 1908, 62, 89.

⁶ Hill, *Chem. News*, 1895, 72, 75.

⁷ Schultz-Sellack, *Ber.*, 1871, 4, 109.

meet the most concentrated acid in the first vessel, and then pass through slightly weaker acid, and so on until the trioxide is completely absorbed. The acid in the last absorption vessel should contain 98 to 99 per cent. H_2SO_4 ; if stronger than this the acid has the same vapour pressure as the trioxide and the latter is not absorbed; if weaker, a mist is formed which is difficult to absorb.¹

Ordinary commercial "oleum" is 20 per cent. oleum, that is, it contains 80 per cent. of H_2SO_4 and 20 per cent. of "free" SO_3 . 100 parts of such "oleum," i.e. 80 parts of H_2SO_4 + 20 parts of SO_3 , can take up $\frac{16}{80} \times 20 = 4.5$ parts of H_2O , yielding $80 + 24.5 = 104.5$ parts of H_2SO_4 . Sulphuric acid containing high percentages of additional sulphur trioxide is frequently manufactured by distilling acid containing 20 to 80 per cent. of the trioxide.

Physical Properties.—Pure pyrosulphuric acid is a colourless crystalline solid² of melting-point 35°C .; the addition of a little water or of sulphur trioxide lowers the melting-point; the colour of the acid is frequently brown, due to the presence of traces of organic matter.

In the following table are given the melting-points for ordinary sulphuric acid containing gradually increasing proportions of additional sulphur trioxide;³ the maxima for pure sulphuric acid and pure pyrosulphuric acid are evident at the values 0 per cent. and near 40 per cent. (see also p. 167).

MELTING-POINTS OF H_2SO_4 - SO_3 MIXTURES.

Percentage SO_3 .	Melting-point, $^\circ \text{C}$.	Percentage SO_3	Melting-point, $^\circ \text{C}$.	Percentage SO_3 .	Melting-point, $^\circ \text{C}$.
0	+10.5	30	+15.2	60	+ 0.7
5	+ 3.5	35	+26.0	65	+ 0.8
10	— 4.8	40	+33.8	70	+ 9.0
15	—11.2	45	+34.8	75	+17.2
20	—11.0	50	+28.5	80	+22.0
25	— 0.6	55	+18.4		

The specific gravity of "fuming sulphuric acid" reaches a maximum in the neighbourhood of 50 to 60 per cent. of "free" trioxide, the composition of maximum density acid being dependent to some extent on the temperature. In the next table⁴ are given figures for the specific gravities of concentrated sulphuric acid and the fuming acid at 15°C ., which show clearly the irregularity in the variation of this physical characteristic with gradual alteration in composition.

Investigation has also been made of the viscosity,⁵ vapour pressure, boiling-point, specific heat, heat of solution in water,⁶ electrical resistance

¹ McDavid, *J. Soc. Chem. Ind.*, 1924, 43, 57 T.

² Marignac, *Ann. Chim. Phys.*, 1853, [iii.], 39, 184.

³ Knietzsch, *Ber.*, 1901, 34, 4102.

⁴ Knietzsch, *loc. cit.*; Messel, *J. Soc. Chem. Ind.*, 1885, 4, 573; Gavelle, *Mon. scient.*, 1913, 3, i., 301.

⁵ Dunstan and Wilson, *Trans. Chem. Soc.*, 1908, 93, 2179.

⁶ Porter, *Trans. Faraday Soc.*, 1918, 13, 373, 389.

SPECIFIC GRAVITIES OF CONCENTRATED AND FUMING SULPHURIC ACIDS.

H ₂ SO ₄ (per cent.).	Total SO ₃ (per cent.).	Free SO ₃ (per cent.).	Sp. Gr. at 15° C.	Sp. Gr. at 45° C.
95.98	78.85	..	1.8418	..
96.68	78.92	..	1.8429	..
96.99	79.18	..	1.8431	..
97.66	79.72	..	1.8484 max.	..
98.65	80.53	..	1.8403	..
99.40	81.14	..	1.8388 min.	..
99.76	81.44	..	1.8418	..
100.00	81.63	0	1.8500	1.822
..	83.46	10.0	1.888	1.858
..	85.30	20.0	1.920	1.887
..	87.14	30.0	1.957	1.920
..	88.97	40.0	1.979	1.945
..	90.81	50.0	2.009	1.964 max.
..	92.65	60.0	2.020 max.	1.959
..	94.48	70.0	2.018	1.942
..	96.32	80.0	2.008	1.890
..	98.16	90.0	1.990	1.864
..	100.00	100.0	1.984	1.814

and capillarity ¹ of fuming sulphuric acid of varying richness in sulphur trioxide.

Chemical Properties.—Pyrosulphuric acid, whether pure or mixed with excess of sulphuric acid or sulphur trioxide, readily undergoes decomposition into sulphuric acid and the trioxide; indeed, the fumes evolved at the ordinary temperature are due to vaporisation of the trioxide from the molten acid or its solution in sulphuric acid. On heating the acid, sulphur trioxide is expelled until the mixture of sulphuric acid and water of minimum vapour pressure (98.3 per cent. sulphuric acid) remains. It is owing to this behaviour that pyrosulphuric acid and "fuming sulphuric acids" in general have no definite and constant boiling temperature.

In consequence of this readiness of "fuming sulphuric acid" to undergo fission into its two constituents, the chemical properties of the acid are largely a blend of those of sulphuric acid and its anhydride.

Platinum ² and lead ³ are attacked more seriously by fuming sulphuric acid than by ordinary sulphuric acid, but of considerable technical value is the fact that although a weaker acid corrodes wrought iron, this metal becomes "passive" in acid containing more than 27 per cent. of "free" anhydride.⁴

The fuming sulphuric acid of commerce contains less sulphur trioxide than corresponds with the formula H₂S₂O₇, and therefore consists of a mixture of pyrosulphuric acid and sulphuric acid.

¹ Knietzsch, *loc. cit.*

² Scheurer-Kestner, *Compt. rend.*, 1878, 86, 1082.

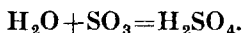
³ Tungay, *Chemical Age*, 1928, 19, 27.

⁴ Knietzsch, *Ber.*, 1901, 34, 4110.

Constitution.—The constitution of pyrosulphuric acid is to be regarded as that of an anhydride of sulphuric acid produced by the elimination from two molecules of the latter of a single molecule of water; the structural formula is therefore $\text{OH} \cdot \text{SO}_2 \cdot \text{O} \cdot \text{SO}_2 \cdot \text{OH}$, where the SO_2 -group possesses the same character as in sulphuric acid.

Estimation.—The estimation of pyrosulphuric acid is generally effected by the addition of water to a definite quantity and determination of the amount of sulphuric acid formed. Various special forms of apparatus have been suggested to obviate loss of the trioxide during the earlier manipulations.¹

The amount of free trioxide in "fuming sulphuric acid" can be estimated by titration with water in a stoppered cylinder. The water is added until no further fuming occurs when air is blown through a glass tube on to the liquid surface.² Each molecule of water added indicates the presence of one molecule of sulphur trioxide, thus :

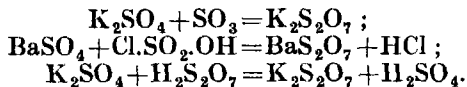


A thermometric method of evaluating the "fuming acid" consists in adding excess of standard 80 per cent. sulphuric acid and titrating back with the "fuming acid"; the temperature of the solution rises with each addition of the "fuming acid" until the water content of the standard is exhausted.³

Pyrosulphates.—The pyrosulphates of the alkali metals are obtained most easily by heating the corresponding acid sulphates to 300° – 350°C :⁴



This dehydration, however, does not proceed to completion even under reduced pressure, and in order to obtain the pure salts it is preferable to allow the finely divided anhydrous normal sulphate to interact with sulphur trioxide.⁵ This latter process stands in fairly close relationship with the methods based on the treatment of a normal sulphate with chlorosulphonic acid,⁶ with the aid of heat, and on the crystallisation of the solution produced by dissolving a normal sulphate in warm "fuming sulphuric acid" :⁷



When heated strongly, for instance above 450°C ., the pyrosulphates undergo decomposition into sulphur trioxide and the corresponding normal sulphate. The sodium salt, which melts at 400.9°C .,⁸ exhibits appreciable dissociation at about 460°C . In contact with moist air or

¹ For example, see Vernon, *Chem. Zeit.*, 1910, 34, 792; Finch, *Zeitsch. Schiess. Sprengstoffwesen*, 1910, 5, 167.

² Parker, *J. Soc. Chem. Ind.*, 1917, 36, 692.

³ Somiya, *Proc. Imp. Acad. Tokyo*, 1927, 3, 76.

⁴ Schultz-Sellack, *Ber.*, 1871, 4, 109; Schulze, *ibid.*, 1884, 17, 2705; Baum, *ibid.*, 1887, 20, 752.

⁵ Cambi and Bozza, *Ann. Chim. Appl.*, 1923, 13, 221.

⁶ Schulze, *loc. cit.*

⁷ Schultz-Sellack, *loc. cit.*

⁸ Cambi and Bozza, *loc. cit.*

water the pyrosulphates become converted into the corresponding acid sulphates :¹



Sulphuric Acid, H_2SO_4 .

This commonest derivative of sulphur trioxide and the most important of all acids from a technical and commercial aspect, has been known from early times, although its production on a large scale and at a low price dates from the success of the "lead chamber" process of manufacture, which revolutionised chemical industry in the early part of the nineteenth century.

Occurrence.—Rivers and springs which have their sources in volcanic regions frequently contain appreciable quantities of sulphuric acid,² the amount rising sometimes to 0.5 per cent.; such waters are found for example in Texas. The free acid is also found in the ground water on the moors near Danzig.³ Certain molluscs, for example, *Dolium galea*, secrete a considerable amount of free sulphuric acid.⁴ Traces are present in the air of towns to the extent of a few thousandths of one per cent.,⁵ but its action on finely divided salt (from sea spray) suspended in the air gives rise to traces of sodium sulphate; the latter is the probable cause of the almost immediate crystallisation of super-saturated solutions of sodium sulphate when exposed to the air.

Sulphates occur abundantly in nature, the chief being those of calcium, barium, strontium, magnesium, aluminium, iron, zinc, copper, sodium and potassium.

Early History.—Although the destructive distillation of partially dehydrated sulphate such as alum was undoubtedly practised very early, even perhaps in the tenth century, the first definite details of the process emanated from Basil Valentine towards the end of the fifteenth century, who described the distillation of green vitriol with silica; the name *oil of vitriol* is derived from this process. Basil Valentine also obtained an acid product by the combustion of a mixture of sulphur and saltpetre, the identity of this "sulphuric acid" with "oil of vitriol" being first proved by A. Libavius in 1595.

Glauber was the first to separate sulphur from the acid, by heating its salts with coal and acidifying the aqueous extract of the product. On account of this relation between sulphur and the acid, the French chemists de Morveau, Lavoisier, Berthollet and Fourcroy proposed the name "sulphuric acid,"⁶ which has been retained.

The first experimental investigation indicating the quantitative composition of the acid was made by Gay-Lussac in 1807.⁷

Formation.—Sulphuric acid is commonly produced in the oxidation of sulphur compounds less rich in oxygen:

(a) Finely divided sulphur in a moist atmosphere undergoes very

¹ Schultz-Sellack, *loc. cit.*; Berthollet, *Compt. rend.*, 1883, 96, 208.

² Fleischer, *Ber.*, 1876, 9, 995; Mallet, *ibid.*, 1872, 5, 817; *Chem. News*, 1872, 26, 147; Pollacci, *Gazzetta*, 1876, 5, 237; Portevin, *Compt. rend.*, 1928, 187, 1148.

³ Schroedter, *Chem. Erde*, 1928, 4, 70.

⁴ Boedeker and Troschel, *Ber. Berlin Akad.*, 1854, p. 486; de Luca and Panceri, *Bull. Soc. chim.*, 1867, [ii.], 9, 400; Maly, *Ber.*, 1880, 13, 820.

⁵ Smith, *Proc. Roy. Soc.*, 1877, 26, 512.

⁶ *Méthode de Nomenclature chimique*, 1787.

⁷ Gay-Lussac, *Mém. Soc. d'Arcueil*, 1807, 1, 215.

slow oxidation, some sulphuric acid being produced ;¹ the oxidation can rapidly be effected by nitric acid or by aqueous solutions of chlorine or bromine.

(b) Sulphur dioxide in a moist condition also readily oxidises to sulphuric acid (see sulphur dioxide and trioxide), the change being aided by the presence of nitric oxide or by contact with finely divided platinum. With aqueous solutions, free oxygen can be replaced by various oxidising agents such as nitric acid, the halogens,² or hydrogen peroxide.

(c) Oxidation of the salts richer in sulphur or poorer in oxygen, for example the polythionates, thiosulphates, hydrosulphites and sulphides, together with their corresponding acids, also produces sulphates as the final stable product.

Manufacture.—The world's annual output of sulphuric acid is approximately 10 million tons, and this huge amount is supplied almost entirely by the "lead chamber" and "contact" processes. The dry distillation of green vitriol as a technical operation has now been abandoned. In Great Britain and Northern Ireland the output for the year 1928 in terms of 100 per cent. sulphuric acid and including oleum was 928,000 tons.³

*The "Lead Chamber Process."*⁴

Historical.—This process had its origin in the early preparation of sulphuric acid by the oxidation of sulphur dioxide with nitric acid, for which operation lead chambers were first introduced in 1746 by Roebuck of Birmingham. In 1793 Clément and Désormes showed that under proper conditions the nitric acid aids the oxidation, which is in the main effected by atmospheric oxygen, and the injection of steam having already been introduced in 1774 by de la Folie, the basal chemical process was much the same as to-day. Gay-Lussac's tower was first suggested by that chemist in 1827 and was first used in 1835, being introduced into Britain in 1844. J. Glover constructed his first tower at Newcastle in 1861.

Until 1888 the sulphur dioxide was obtained entirely from free Sicilian sulphur, but on account of increasing price iron pyrites was substituted, and by 1862 free sulphur was practically no longer used. The abundant output of American sulphur has of recent years revived the employment of sulphur, which now to an ever-increasing extent is displacing iron pyrites as the chief source of sulphur dioxide. Other metallic sulphides which necessitate a preliminary roasting in their metallurgical treatment, for example zinc blende, also serve as subordinate sources of sulphur dioxide, but with such materials it is necessary that fluorine should first be removed from the gases by passing the latter up a tower packed with quartz.⁵

Of the total output of sulphuric acid in Great Britain and Northern Ireland during 1928 (see above), 49 per cent. was produced from pyrites,

¹ Maly, *Monatsh.*, 1880, 1, 205 ; Wagenmann, *Ann. Phys. Chem.*, 1832, [ii.], 24, 601.

² For the action of chlorine on moist sulphur dioxide, see Neumann and Wilczewski, *Zeitsch. angew. Chem.*, 1923, 36, 377.

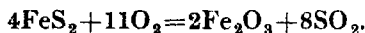
³ *Chem. Trade J.*, 1929, 85, 565.

⁴ For details of the commercial processes for sulphuric acid manufacture special books must be consulted, for example, various volumes of the series entitled *Manufacture of Acids and Alkalis*, Lunge and Cumming (Gurney & Jackson, 1923) ; also *Gli Acidi Inorganici*, Aita and Molinari (Milan, 1928).

⁵ Prost, *Chem. Zeit.*, 1902, 12, 25.

over 24 per cent. from "spent oxide," 17.56 per cent. from sulphur, and 9.26 per cent. from zinc concentrates.¹

The Pyrites Burners.—In the lead chamber process the first chemical action is the oxidation of sulphur to sulphur dioxide by atmospheric oxygen. The iron pyrites (or free sulphur, "spent oxide" from the gas works, or other sulphides such as zinc blende, as the case may be) is placed on shelves or bars in a series of ovens of suitable type. When iron pyrites or sulphur is used, the combustion when once started proceeds to completion without further assistance by external heat :



The supply of air, which is drawn through the "burners" by suction, is so adjusted that sufficient oxygen will be present to oxidise the sulphur dioxide subsequently to sulphuric acid and also finally to leave the oxides of nitrogen (see the following) in approximately the composition represented by the formula N_2O_3 .

The Glover Tower.—From the pyrites burners the gases pass through a flue for the collection of dust and then at a temperature of approximately 350°C . enter the bottom of the Glover tower. This lead tower, about thirty feet high and lined with stoneware, is packed with some resistant material such as flints, or more frequently in modern practice with a specially prepared filling, for example small hollow stoneware cylinders. By means of a distributing device, dilute sulphuric acid (about 65 per cent.) from the chambers ("chamber acid") and concentrated sulphuric acid containing dissolved oxides of nitrogen from the Gay-Lussac tower (see the following) are introduced at the top of the Glover tower and trickle down over the filling material, thus exposing a large surface to the ascending current of hot gases; the Gay-Lussac tower acid thereby gives up its oxides of nitrogen, whilst the dilute acid becomes concentrated; the acid which issues from the bottom of the Glover tower has a temperature of 120° to 130°C . and contains roughly 80 per cent. of pure acid.

Another purpose served by the Glover tower is that it relieves the lead chambers of the production of part of the acid, and it may account for as much as 16 per cent. or more of the total yield of acid, due to the conversion of sulphur dioxide into sulphuric acid inside the tower; indeed, a tower of similar type is sometimes interposed between two of the chambers with a view to the same result.²

The capacity of the Glover tower is usually $2\frac{1}{2}$ to 3 per cent. that of the chambers, and in order to obviate the need for inconveniently large towers, two are sometimes employed in series.

With a view to remedying any shortage in the supply of oxides of nitrogen from the Gay-Lussac tower, due to unavoidable loss, a little nitric acid is introduced into the gaseous mixture, usually down the Glover tower but sometimes, although less frequently, by placing pots containing nitre and sulphuric acid in the flue between the pyrites burners and the Glover tower. In some cases the oxides of nitrogen are supplied by the catalytic oxidation of ammonia, the platinum catalyst being electrically heated.³

¹ *Chem. Trade J.*, 1929, 85, 565.

² Gilchrist, *J. Soc. Chem. Ind.*, 1899, 18, 459; *J. Amer. Chem. Soc.*, 1893, 15, 624; 16, 438; Kestner, *J. Soc. Chem. Ind.*, 1903, 22, 333; Hart and Bailey, *ibid.*, 1903, 22, 473; Porter, *ibid.*, 1903, 22, 476.

³ Adam, *Chem. Trade J.*, 1918, 62, 181.

The Lead Chambers.—On leaving the Glover tower the gaseous mixture of sulphur dioxide, oxygen, nitrogen oxides and atmospheric nitrogen, now cooled to 90°C ., passes into the lead chambers. These are constructed of sheet lead ¹ about 3 mm. thick; the walls and roof are sealed together by a blowpipe flame, the edges of the base being turned up so as to form a flat dish in which the acid collects and forms a gas-tight seal between the base and the sides. The whole chamber is supported in a wooden framework on pillars so that each part is accessible,² the exposure to the atmosphere also aiding cooling. Chambers frequently exceed 40,000 cubic feet in individual capacity and a series of three or four is commonly used, the gases being conducted from one to the other as well as to and from the chamber system by lead pipes.

Much depends on the proper construction of the chambers; they may be rectangular or circular, the latter possessing the advantage of allowing more complete mixing with the steam, the gases being introduced at the side tangentially and then moving spirally until the central exit is reached. It is mainly on account of the success attained by the use of the more modern forms of chambers that the chamber process is still able to remain in vigorous existence.

Steam, or water in the form of very fine spray, is injected into the chambers, sulphuric acid being formed and falling as a drizzle to the floor, whilst the oxides of nitrogen, having exercised their influence on the reaction between sulphur dioxide, oxygen and water (see the following), pass away with the atmospheric nitrogen. Dilute sulphuric or nitric acid or a solution of nitrous oxides in sulphuric acid (density 1.59) may be sprayed into the chamber ³ instead of water or steam; there are advantages, however, in using cold water, since besides effecting an economy in nitre or nitric acid, the lower working temperature is suitable for a satisfactory reaction. It is unnecessary to go to the expense of raising steam in order to condense it again in the chambers.

Great care is required in regulating the process in the chambers; the gases need to be well mixed; they must not be allowed to attain too high a temperature during the reaction, and they must not emerge too soon from the chambers. The supply of water or steam has also to be adjusted carefully, too much causing an unnecessarily dilute acid and also tending to induce an excessive reduction of the oxides of nitrogen to nitrous oxide or even to nitrogen, whereas too little will give rise to an acid so concentrated that the lead is seriously attacked and the life of the chambers, which should be from 10 to 20 years, considerably shortened. The concentration of the oxides of nitrogen present is also an important factor influencing the yield of sulphuric acid obtained.

Lead-covered towers ("plate towers") fitted internally with perforated stoneware plates are sometimes interposed between the chambers, or the latter may in part be replaced by a series of smaller absorption boxes divided longitudinally into three narrow compartments by means of perforated walls,⁴ the gases entering the middle compartment and leaving from the side compartments. Such arrangements not only aid

¹ On the use of lead as a constructional material, see Tungay, *Chemical Age*, 1928, 19, 27.

² For an account of a repair during operation, see Kendrick and Souder, *Ind. Eng. Chem.*, 1927, 19, 964.

³ Fischler, *Zeitsch. angew. Chem.*, 1926, 39, 55; Moritz, *French Patent*, 593627 (1925); *British Patent*, 285847 (1927). See also Spangler, *Ind. Eng. Chem.*, 1929, 21, 417.

⁴ Barth, *German Patent*, 446398 (1923).

the blending of the gases, but also allow more than an equivalent reduction in the capacity of the chambers.¹

The Gay-Lussac Tower.—On leaving the chambers the gases contain only traces of sulphur dioxide, and are red in colour on account of the presence of the oxides of nitrogen. The latter are removed by leading the mixture to a circular tower, or sometimes two towers, the height of which may be 26 to 65 feet and the capacity about 4 per cent. that of the chambers. For convenience in the arrangement of the works the Gay-Lussac towers are usually built near the Glover tower.

Down the towers and over the filling of hard coke or other material there trickles sulphuric acid of 80 per cent. concentration, for example,

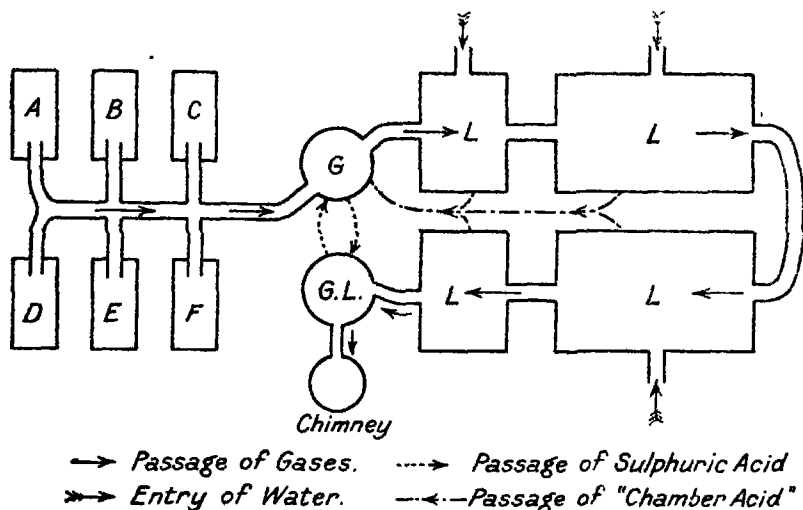


FIG. 9.—Diagram illustrating the "Lead Chamber Process."

A, B, C, D, E, F, Pyrites Burners; G, Glover Tower; G.L., Gay Lussac Tower, L, Lead Chambers.

acid from the Glover tower, which absorbs the mixture of nitrogen dioxide and nitric oxide from the ascending gases; the solution thus obtained is then pumped to the top of the Glover tower, in which the oxides of nitrogen are again taken up by the gaseous current and once more find their way to the chambers. With perfect working, the gas issuing from the Gay-Lussac tower will consist of almost pure nitrogen, and is led away into the factory chimney. A water scrubber is sometimes placed between the two Gay-Lussac towers;² the water converts

¹ See further, Lütj, *Zeitsch. angew. Chem.*, 1905, 18, 1253; Rabe, *ibid.*, 1735; Schliebs, *ibid.*, 1900; Hüppner, *ibid.*, 2001; Niedenfür, *ibid.*, 1906, 19, 61; Hartmann and Benker, *ibid.*, 132, 1125; Coleman, *J. Soc. Chem. Ind.*, 1905, 24, 482; Forrer, *Bull. Soc. chim. Belg.*, 1922, 31, 254; Briner and Rossignol, *Helv. Chim. Acta*, 1923, 6, 647; Harvey, *Chem. Met. Eng.*, 1929, 36, 402. See also *British Patents*, 247644 (1924); 206047 (1925); 262397 (1926); *German Patent*, 416859 (1924); *Austrian Patent*, 106847 (1926). For a description of a small scale plant for the intensive production of sulphuric acid, see Perley, *Ind. Eng. Chem.*, 1929, 21, 202. For the use of the Schmiedel Box, see Bush and Grounds, *Trans. Inst. Chem. Eng.*, 1927, 5, 34. For a description of the Mills-Packard Chamber Plant, see Mills, *ibid.*, p. 42.

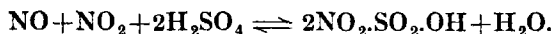
² Skoglund, *U.S. Patent*, 1,559,292 (1925).

nitrogen dioxide into nitric acid (in solution) and nitric oxide, and the latter after reoxidation is absorbed in the last tower.

There is, however, some loss of the valuable nitrous gases, necessitating the introduction of small quantities of nitric acid at or before the Glover tower or into the chamber itself (see before); the loss is probably due mainly to the reduction of the oxides to nitrous oxide and even nitrogen, which are not absorbed in the Gay-Lussac tower.¹

The natural draught of the factory chimney was at one time found sufficient for the movement of the gases through the plant, but to-day suitable fans are commonly installed to aid the circulation.

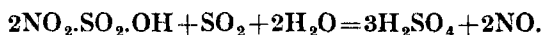
Theory of the Action in the Gay-Lussac and Glover Towers.—The gases issuing from the chambers consist mainly of nitrogen dioxide, nitric oxide and atmospheric nitrogen. The two former are dissolved by the sulphuric acid in the Gay-Lussac tower with formation of a solution of nitrosylsulphuric acid in excess of sulphuric acid (see also below):



Occasionally the resulting acid solution is violet in colour, due to the presence of the unstable sulphonitronic acid (p. 251), and it then readily decomposes with effervescence of nitric oxide.

As the formation of nitrosylsulphuric acid is a reversible process, dilution of the sulphuric acid solution in the Glover tower tends to cause hydrolysis, which is aided by the high temperature; the oxides of nitrogen resulting from the decomposition pass on with the sulphur dioxide and excess of air to the chambers, whilst the sulphuric acid descends and issues at the bottom of the tower.

In addition to the foregoing process, however, the Glover tower actually produces sulphuric acid. This is brought about by interaction of the sulphur dioxide in the burner gases with nitrosylsulphuric acid, as follows:



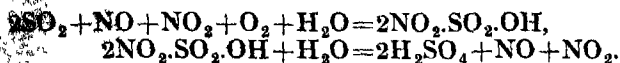
Theory of the Action in the Lead Chambers.—The actual mechanism of the chemical process in the lead chambers has for years been a matter of much conjecture and controversy. The formation of unstable intermediate compounds which subsequently undergo decomposition with production of sulphuric acid is almost universally accepted, but unfortunately there is no general agreement as to the identity of the intermediate compound or compounds.

G. Lunge favoured a view, first put forward by H. Davy in 1812, that sulphur dioxide, water, oxygen and nitrogen trioxide (or a mixture of nitric oxide and nitrogen dioxide) interact with formation of nitrosylsulphuric acid (p. 247), which subsequently undergoes decomposition by water producing sulphuric acid and reproducing "nitrogen trioxide"; the latter is then able once more to give rise to nitrosylsulphuric acid.²

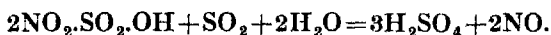
¹ Inglis, *J. Soc. Chem. Ind.*, 1907, 26, 668; 1906, 25, 149; Carpenter and Linder, *J. Soc. Chem. Ind.*, 1902, 21, 1490; Hempel and Heymann, *Zeitsch. Elektrochem.*, 1906, 12, 600; Graire, *Compt. rend.*, 1925, 180, 292. See further, Petersen, *British Patent*, 249914 (1924); Krafft, *U.S. Patent*, 1611534 (1926).

² Lunge, *Trans. Chem. Soc.*, 1885, 47, 465; *Chem. News*, 1888, 57, 69; *Ber.*, 1885, 18, 1384; 1888, 21, 67, 3223; *Zeitsch. anorg. Chem.*, 1894, 7, 212; Winkler, *Zeitsch. Chem.*, 1899, p. 715; Schertel, *Trans. Chem. Soc.*, 1860, 12, 80; *Ber.*, 1889, 2, 542; Sorel, *Zeitsch. angew. Chem.*, 1889, p. 2647; Neumann, *ibid.*, 1906, 19, 1702.

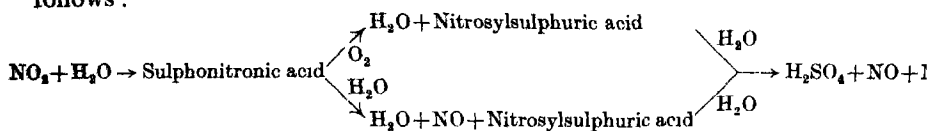
The cycle of changes proceeds until all the sulphur dioxide and oxygen are consumed :



In the first chamber, and also in the Glover tower, the gases are usually colourless, and it is possible that the excess of sulphur dioxide here causes a reduction to nitric oxide :



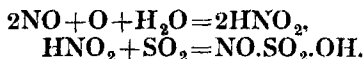
More recently this theory has been modified by the introduction of another intermediate product, namely the violet or blue sulphonitronic acid (see p. 251) which is supposed to precede the formation of the nitrosylsulphuric acid. The series of changes is then represented as follows :



the sulphonitronic acid undergoing conversion by oxygen or water into nitrosylsulphuric acid, which is then decomposed by water giving sulphuric acid.¹ This theory loses somewhat in attractiveness, however, on account of the uncertainty of the composition of the sulphonitronic acid.

Free nitrosylsulphuric acid actually occurs in the lead chambers only under abnormal conditions of working ; its separation as " chamber crystals " is most undesirable from the manufacturer's point of view, as not only does it indicate improper regulation of the process, but it also causes the lead walls of the chambers to be attacked unduly. A solution of " violet acid " is sometimes obtained at the bottom of the Gay-Lussac tower.

An alternative explanation proposed by F. Raschig, who also regarded nitrogen trioxide or nitrous acid as the form in which the nitrogen oxides are active, is based on the primary formation of a hypothetical nitrososulphonic acid, as represented by the equations :



The nitrososulphonic acid then reacts with a second molecule of nitrous acid, producing the purple sulphonitronic acid. As stated earlier, the composition of this acid is uncertain, but assuming the formula H_2SNO_5 , the equation for the reaction is



whilst the final reaction yielding sulphuric acid is



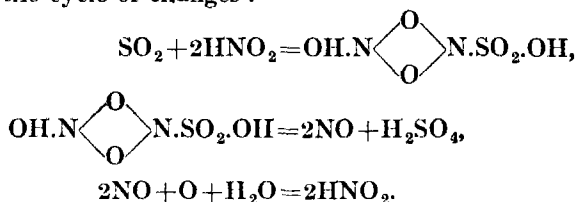
¹ Lunge and Berl, *Zeitsch. angew. Chem.*, 1906, 19, 807, 837, 881 ; 1907, 20, 1713 ; 1910, 23, 2241 ; Reynolds and Taylor, *J. Soc. Chem. Ind.*, 1912, 31, 367. See also Wentzki, *Zeitsch. angew. Chem.*, 1911, 24, 392, 1468.

² Raschig, *Annalen*, 1887, 241, 161 ; 1888, 248, 123 ; *Zeitsch. angew. Chem.*, 1904, 17, 1398, 1777 ; 1905, 18, 1281 ; 1907, 20, 694 ; *J. Soc. Chem. Ind.*, 1911, 30, 166.

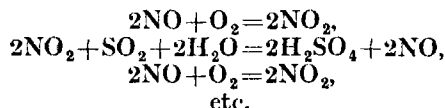
An advantage possessed by this series of changes is that it explains more satisfactorily than the preceding theory why much sulphuric acid can be formed in the Glover tower. In the lead chambers the acid formed is so weak that the nitrososulphonic acid stage is possibly absent from the series.

The preceding views have been subjected to much criticism,¹ both mutual and independent. Manchot² regards the "blue acid" as an oxide of composition between $\text{NO}_{1.5}$ and NO . The formula H_2SNO_5 suggested by Raschig is improbable, as the absorption spectrum is not in any way similar to that of the compound $\text{CuSO}_4\cdot\text{NO}$ or $\text{FeSO}_4\cdot\text{NO}$. A modification³ of Raschig's theory, whilst avoiding the two foregoing hypothetical acids, postulates the transient formation of yet another unknown acid. Nitrous acid and sulphur dioxide are supposed to

condense to a "nitroxysulphuric acid," $\text{OH}\cdot\text{N} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{N}\cdot\text{SO}_2\cdot\text{OH}$, which immediately decomposes into sulphuric acid and nitric oxide; the latter by uniting with more oxygen and water yields nitrous acid, which re-enters the cycle of changes:



At the present time there is a tendency to a reversion to a simpler conception of the changes involved in the production of sulphuric acid. Already in 1844 Pélégot had suggested that the oxides of nitrogen act simply as "oxygen carriers," thus:



It appears quite likely that the more complicated explanations referred to may be due to some confusion of less simple side reactions with a simple main reaction.⁴ Even at temperatures below 60°C ., nitrogen dioxide is able to oxidise sulphur dioxide to sulphur trioxide, whilst nitric oxide readily combines with the latter to give the compound $2\text{SO}_3\cdot\text{NO}$, which is readily decomposed by water giving sulphuric acid and nitric oxide.

¹ Littmann, *Zeitsch. angew. Chem.*, 1906, 19, 1177; Feigenson, *Chem. Zeit.*, 1906, 30, 851; Manchot, *Zeitsch. angew. Chem.*, 1912, 25, 1055; Wentzki, *ibid.*, 1911, 24, 392; 1914, 27, 312; Trautz, *ibid.*, 1904, 17, 1552; Hempel, *ibid.*, 1914, 27, 218, 407.

² Manchot, König and Reimlinger, *Ber.*, 1926, 59, [B], 2672.

³ Divers, *J. Soc. Chem. Ind.*, 1911, 30, 594; also 1904, 23, 1178. An investigation by Bailey (62nd Ann. Rept. on Alkali, etc. Works, 1926, 12) on the interaction of the oxides of nitrogen with sulphurous acid in the presence of varying concentrations of sulphuric acid supports this view.

⁴ Pélégot, *Ann. Chim. Phys.*, 1844, [iii.], 12, 263; Lunge and Naef, *Chem. News*, 1884, 49, 13; Naef, *Ber.*, 1885, 18, 603; Briner and Kuhne, *Compt. rend.*, 1913, 157, 450; *Annual Reports Chem. Soc.*, 1912, 9, 45; Manchot, König and Reimlinger, *loc. cit.* See also Coleman, *J. Soc. Chem. Ind.*, 1906, 25, 1201.

Until stronger and more convincing evidence is forthcoming as to the formation of the major portion of the sulphuric acid from unstable nitrogen-sulphur oxyacids in the chambers, the only really satisfactory course for general purposes is to adhere to the simple view formulated in the immediately preceding series of equations. Even if these should prove not to show accurately the actual intermediate stages, they do at least represent truly not only the first and last stages of the process with respect to sulphur dioxide and oxides of nitrogen, but also the general nature of the change by which the sulphuric acid is produced.

Subsequent Treatment of the Acid.—The acid from the Glover tower generally contains flue dust (largely ferric oxide), on which account it is used up in the acid factory itself, part being returned to the Gay-Lussac tower and part being used for the preparation of sodium sulphate. For this reason it is not essential that pure nitric acid should be introduced at the Glover tower, and frequently an aqueous solution of the cheaper sodium nitrate is used in its place.

The remaining "chamber acid," containing 68 to 70 per cent. of H_2SO_4 , is concentrated in a series of lead pans (heated on the "counter-current" principle), when water vapour passes off. When a concentration of 77 to 80 per cent. has been attained it is inadvisable to proceed further with the lead pans as the metal begins to reduce the acid. Until the beginning of the present century the subsequent concentration was carried out in porcelain, glass or platinum (gold-lined) retorts, or in a Kessler apparatus. Glass retorts have fallen into disfavour on account of their easy fracture on contact with the hot fire gases, whilst platinum is very expensive. The Kessler method, which is very successful in plants of moderate output, consists in passing hot gases from a coke producer over the acid contained in a shallow flat dish made of volvic stone, and then through a series of superimposed trays luted with acid; the weak acid passes downwards through the trays, meets the hot gases, and arrives at the bottom tray in a highly concentrated condition.

In 1906, Gaillard introduced a system of acid concentration,¹ now extensively used, which has proved efficient and can be adapted (by multiplication of units) to any scale of acid production.

The weak acid (70 per cent.) is atomised in a fine mist down a tower built of obsidianite or acid-proof bricks (see fig. 10), up which hot gases from the combustion of producer gas are ascending. These gases enter at a temperature of 750° to $800^\circ\text{C}.$, and after passing through the tower, which acts as a flue, pass on to a smaller tower of similar design (a recuperator), down which atomised acid undergoes a preliminary concentration before being fed to the main tower. The gases leave the recuperator at about $120^\circ\text{C}.$ and pass to a scrubber, generally a lead-lined rectangular chamber or tower, the bottom of which is paved with acid-proof bricks. The scrubber is packed with coke, the resistance of which to the passage of the gas causes condensation of the acid carried over and removes any foreign matter, which forms a slime on the surface of the coke. The condensed acid is conveyed to the feed tank of the main tower; the gases pass to the exit pipe, the draught through the system being produced by high pressure fans.

The volume of acid passed down the recuperator is approximately

¹ See Parkes and Coleman, *J. Soc. Chem. Ind.*, 1921, 40, 257 T; Parkes, *The Concentration of Sulphuric Acid*, Manufacture of Acids and Alkalis Series, Lunge and Cumming (Gurney & Jackson, 1924).

half that fed to the main tower. The acid flows out of the recuperator at about 150° to 160° C., runs through a water-cooled trough to a lead cooler, where the temperature is reduced to 50° C., and then flows to the feed tanks of the main tower.

Instead of the foregoing type of recuperator, a packed tower working on the Glover principle is sometimes used.

The acid leaving the main tower runs through a mud-catcher to a cooler and thence to the storage tanks. The concentration normally attained is 94 to 95 per cent.

A method due to Strzoda¹ consists in passing the acid, after concentration in open lead pans, downwards through a series of vertical pipes heated externally by producer gas. The vapours evolved are passed through a cooling tower packed with suitable material, and the dilute acid recovered is passed back to the concentrating pipes.

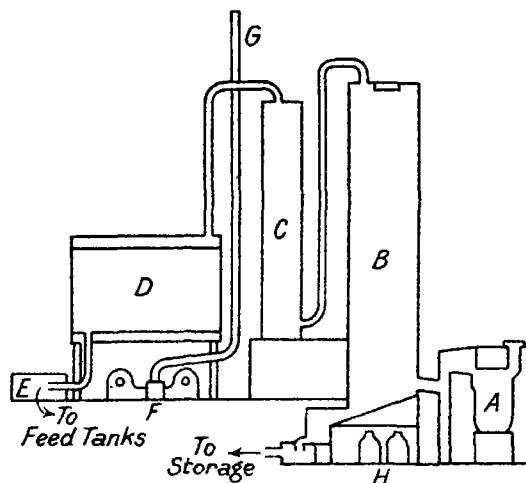


FIG. 10.—Gaillard Concentration Plant.

- | | | |
|----------------|--------------|-----------------------|
| A Furnace. | E Tank. | H Eggs receiving acid |
| B Main tower. | F Fans. | from tanks and |
| C Recuperator. | G Exit pipe. | passing it to |
| D Scrubber. | | atomizers. |

The limit of concentration attainable by any of the foregoing methods is about 98 per cent. If acid of higher concentration than this is required, acid of 97 to 98 per cent. strength can be partially frozen,² when the colourless prisms which separate contain 99.5 to 100 per cent. H_2SO_4 and constitute the frequently so-called, but misnamed, "monohydrate."

Owing to the success of the "contact process" for the preparation of sulphur trioxide and of fuming sulphuric acid, the production of highly concentrated sulphuric acid has been rendered so simple a matter that concentration of the lead chamber acid is of diminished importance. The main value of the chamber process lies in its economical production of a not necessarily very concentrated acid. There are indications, however, that by a suitable combination of the two processes, an even more economical production of concentrated acid may be obtainable (see p. 162).

¹ Strzoda, *Chem. Zeit.*, 1927, 51, 525.

² Morancé, *Compt. rend.*, 1909, 148, 842.

Impurities and their Removal.—At one time sulphuric acid for special purposes was purified from non-volatile foreign substances by distillation, but the process was so expensive, particularly as regards breakage of the retorts if of glass or porcelain, or their depreciation if of platinum, that distillation of the acid has now been abandoned as a technical process.

Arsenic, arising from the fumes of arsenious oxide produced in the combustion of impure pyrites, is the commonest impurity in the chamber acid.¹ As the presence of this element is especially dangerous in acid destined for use in the preparation of foodstuffs, as for example glucose, the acid is purified usually by dilution and treatment with hydrogen sulphide² or a metallic sulphide, for instance barium sulphide,³ or with a thiosulphate, for example barium thiosulphate;⁴ the arsenic is precipitated as sulphide and removed before the final concentration. An alternative but less frequently adopted procedure is to remove the arsenic as the volatile arsenious chloride by adding hydrochloric acid or a chloride and heating gently.⁵ In the concentration of sulphuric acid by freezing (see p. 157), practically the whole of any arsenic present remains in the liquid.

A recently adopted method⁶ for minimising the amount of arsenic in the acid is to pass the gases through a closed vessel placed between the Glover tower and the chambers and containing an oxidising agent such as nitric acid, which will retain the arsenic.

Nitrogen Oxides form another common impurity in crude sulphuric acid; their presence may be detected by the formation of a deep blue coloration on the addition of a little diphenylamine, or by the production of an azo-dye coloration on treating the diluted acid with suitable reagents such as *m*-phenylenediamine or a mixture of sulphanilic acid and α -naphthylamine. In the presence of dissolved nitrogen oxides a "brown ring" test can also be made by carefully adding ferrous sulphate solution. Oxides of nitrogen which, if the acid is not too weak, are present in the form of nitrosylsulphuric acid, can be removed by the introduction of the requisite quantity of ammonium sulphate,⁷ as first recommended by Pelouze;⁸ during the subsequent concentration the nitrogen is rapidly eliminated in the free state by a reaction analogous to the decomposition of ammonium nitrite:



In the laboratory sulphuric acid can be freed from nitric acid by agitation with mercury in a Lunge nitrometer.⁹

Lead Sulphate, which is soluble to a considerable extent in concentrated sulphuric acid, can be removed almost completely by dilution, when it is slowly precipitated.

¹ For a method for the rapid estimation of arsenic in sulphuric acid, see Périgrin, *Ann. Chim. anal.*, 1917, 22, 24.

² See Cory, *Chem. Trade J.*, 1918, 62, 89.

³ Ducher, *Ber.*, 1890, 23, 32.

⁴ Thorn, *Dingl. poly. J.*, 1875, 217, 495; Wagner, *ibid.*, 1875, 218, 321.

⁵ Buchner, *Annalen*, 1855, 94, 241; 1863, 130, 249; Selmi, *Gazzetta*, 1880, 10, 40. See also Scheringa (*Pharm. Weekblad*, 1920, 57, 421), who recommends heating with sulphite, followed by dilution and electrolysis.

⁶ *Austrian Patent*, 106847 (1926).

⁷ Lunge and Abenius, *Zeitsch. angew. Chem.*, 1894, p. 608.

⁸ Pelouze, *Ann. Chim. Phys.*, 1835, 2, 60, 152.

⁹ Steenberg, *Chem. Weekblad*, 1917, 14, 647.

The preceding impurities, as also others such as *antimony* and *selenium*, can all be eliminated by dilution and treatment with hydrogen sulphide, followed by a short heating of the resulting clear acid with a sufficient quantity of ammonium sulphate; in special cases this treatment might be followed by distillation or by recrystallisation of the "hydrate" H_2SO_4 (see p. 157).¹ The presence of selenium in sulphuric acid may be detected by the addition of aspidospermine, when an intense violet coloration develops,² no colour being given by the pure acid. At the present day, however, acid of an extremely high degree of purity is not expected from the lead chamber process.

*The "Contact Process."*³

Although the commercial manufacture of sulphur trioxide and sulphuric acid by the catalytic process has attained success only in comparatively recent years, a patent was acquired in 1831 by P. Phillips of Bristol for the production of sulphuric acid in this way, the suggested catalyst being platinum.⁴ The commencement of the twentieth century saw the main difficulties overcome and the installation of an economical and commercial process in Germany. Since then the number of plants has increased largely and various modifications have been introduced in many countries.

The most active catalyst is platinum applied in finely divided form, for example platinised asbestos. Certain elements, especially arsenic and mercury, have a powerful effect in reducing the activity of the platinum, a quantity of arsenic equal to 0.2 per cent. of the weight of the platinum reducing the activity by 50 per cent.⁵ These "poisons," as they are termed, also include less harmful substances such as antimony, lead, bismuth, etc. The presence of small quantities of rhodium, iridium or osmium in the platinum also causes diminished yields of trioxide, but the presence of palladium or ruthenium has the opposite effect.⁶

Sulphur or iron pyrites again serves as the source of sulphur dioxide, the former being preferable as many of the undesirable impurities are present in pyrites. When using pyrites, investigation has shown that most of the arsenious oxide is to be found in the fumes of the sulphur trioxide which is formed; steam or fine water spray is therefore injected, when the fumes form a mist of dilute sulphuric acid which encloses the arsenious oxide together with other dust, and can be condensed by passing the gas through a series of lead pipes.⁷ Subsequently the gases are dried by passing up a series of towers down which concentrated sulphuric acid is made to trickle. Tests are then made to ensure the

¹ Moddermann, *Zeitsch. anal. Chem.*, 1882, 21, 218; Hayes, *Dingl. poly. J.*, 1848, 110, 104.

² Palet, *Anal. Soc. Quim. Argentina*, 1917, 5, 121.

³ For an historical account, together with an examination of the physical properties of "mixtures" of sulphur trioxide and water in varying proportions, see Knietsch, *Ber.*, 1901, 34, 4069. See also Meyer, *J. Soc. Chem. Ind.*, 1903, 22, 348; Stone, *ibid.*, 350; Reese, *ibid.*, 351; Budnikov, *Chem. Zeit.*, 1927, 51, 209, 230.

⁴ Phillips, *British Patent*, 6096 (1831). See also Magnus, *Annalen*, 1832, [ii.], 24, 610.

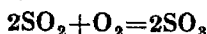
⁵ Maxted and Dunsby, *J. Chem. Soc.*, 1928, p. 1600.

⁶ Levi and Faldini, *Giorn. Chim. Ind. Appl.*, 1927, 9, 223. For the effect of X-rays on the platinum catalyst, see Clark, McGrath and Johnson, *Proc. Nat. Acad. Sci.*, 1925, 11, 646.

⁷ For an electrical type of purifier, see *French Patent*, 624913 (1926).

absence of impurities from the gases and the presence of a sufficient excess of oxygen.¹

The reaction



is accompanied by a considerable evolution of heat, but, as has already been stated, the formation of trioxide is incomplete above 450° C.

(p. 136).² For this reason the contact chambers (see fig. 11), containing a group of vertical tubes in which are placed small horizontal sieves to support the platinised asbestos and prevent it becoming unduly compressed, are maintained near 400° C. In order to prevent the chambers being overheated by the liberation of heat in the chemical change, the cool entering gases are first circulated round the outside of the contact tubes; by this device not only is the temperature inside the tubes maintained constant, but the gaseous mixture is also preheated to a suitable degree before meeting the contact material. Instead of asbestos, anhydrous magnesium sulphate or other material may be used as a platinum carrier; in such cases, in order to ensure the availability of the platinum, the carrier should first be saturated with alcohol, dipped into an alcoholic solution of the platinum compound, quickly dried and ignited. Useless deposition inside the carrier is thus prevented.³

After the gaseous mixture has traversed one or more chambers, the sulphur trioxide is absorbed by sulphuric acid usually maintained at 97 to 99 per cent. concentration⁴ by regulated dilution with weaker acid or water. Acid of this concentration possesses the double advantage of being usable in iron pots and of absorbing the anhydride better than water, which causes fumes of sulphuric acid, and better than stronger acid, which leaves some sulphur trioxide unabsorbed. If fuming acid is required, the absorbent is generally maintained at a content of 27 to 40 per cent. of "free" anhydride, acid of this strength also leaving iron unattacked.

Should the platinum become "poisoned," that is, rendered inactive by contamination with impurities which have escaped the initial purification process, it can generally be revived by heating in a current of a reducing gas such as hydrogen. Safety precautions for the operators are desirable during the process.⁵

¹ For the treatment of zinc blende roaster gases for use in the Contact Process, see Robson, *Trans. Canad. Inst. Min. and Met.*, 1927, 30, 950; and for the use of gases produced in the bessemerising of nickel-copper matte, see De Blois, *ibid.*, p. 929.

² For the influence of the reaction rate in the Contact Process, see Lewis and Ries, *Ind. Eng. Chem.*, 1927, 19, 830.

³ von Artner, *German Patent*, 440338 (1926).

⁴ Knietzsch, *loc. cit.*; Sackur, *Zeitsch. Elektrochem.*, 1902, 8, 77.

⁵ Kershaw, *Ind. Eng. Chem.*, 1920, 21, 762.

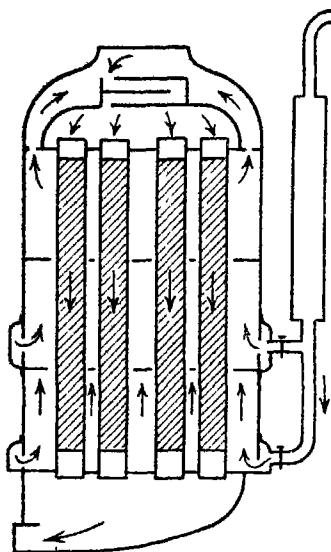
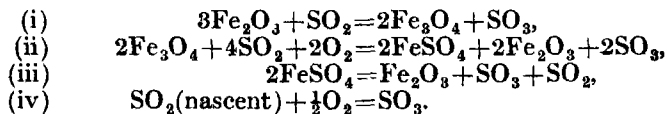


FIG. 11.—Contact Chamber.

Although platinum is the most effective catalyst for this reaction, other catalysts are known,¹ including many oxides and sulphates. Ferric oxide² in the form of pyrites ash has proved capable of technical application, but on account of its lower activity, a somewhat higher temperature, usually near 550° C., is necessary. At this temperature the formation of trioxide is not complete, and therefore, after the removal of the trioxide from the iron oxide contact chamber, the issuing gases are passed through a platinum contact chamber at a lower temperature, where the reaction is completed. Such an arrangement possesses an advantage arising from the fact that the catalytic action of ferric oxide is not adversely influenced, but even improved, by the presence of arsenic;³ the crude combustion gases therefore no longer need careful purification, this being effected by the iron oxide itself.

Other forms of apparatus have been constructed or proposed to employ ferric oxide as the sole catalyst. In one scheme, use is made of the power of ferric oxide containing ferrous compounds to absorb sulphur dioxide. The ferric oxide impregnated with ferrous sulphate gradually descends an inclined rotating flue up which passes the usual mixture of sulphur dioxide and air. By the heat of the gaseous mixture the descending solid is maintained near 350° C. at the upper end of the flue, and at the temperature of its optimum catalytic effect, namely 550° C., at the lower end. Sulphur trioxide is produced by incomplete combination of sulphur dioxide and oxygen in the lower portion of the flue, whilst the uncombined sulphur dioxide, being largely absorbed by the cooler mass higher in the flue, is returned to the hotter region, where it becomes expelled and is thus given another opportunity of conversion into trioxide. As no precautions are taken to exclude moisture, the vapours issuing from the top of the flue can be condensed directly to fuming sulphuric acid.

It is probable that the mode of action of platinum and possibly also that of the metallic oxides as catalysts is by surface adsorption of the sulphur dioxide, this gas being thus brought into a condition more favourable to reaction.⁴ As regards the action of the metallic oxides, however, the view that it depends on alternate oxidation and reduction has recently been developed. Thus it is assumed that in the case of iron oxide the following reactions occur:⁵



The fact that ferrous sulphate above 605° C. decomposes to yield the products given in (iii), and that small quantities of ferrous sulphate are

¹ Lunge and Reinhardt, *Zeitsch. angew. Chem.*, 1904, 17, 1041; Küster, *Zeitsch. anorg. Chem.*, 1904, 42, 453; Keppeler, *Zeitsch. angew. Chem.*, 1902, 15, 809. Diaspore has recently been employed on a manufacturing scale, see *U.S. Patent*, 1605088 (1926).

² Keppeler, *Zeitsch. angew. Chem.*, 1908, 21, 532, 577; Verola, *French Patent*, 594078 (1924); Kudoh, *British Patent*, 258974 (1925).

³ Lunge and Pollitt, *Zeitsch. angew. Chem.*, 1902, 15, 1105; Berl, *Zeitsch. anorg. Chem.*, 1905, 44, 267; *Zeitsch. angew. Chem.*, 1905, 18, 252. See also Küster, *loc. cit.*

⁴ Wohler, Plüddemann and Wohler, *Zeitsch. physikal. Chem.*, 1908, 62, 641; Bodenstein and Fink, *ibid.*, 1907, 60, 1, 46; Bodenstein, *ibid.*, 1929, [B], 2, 345. See also Wieland, *Ber.*, 1912, 45, 679, 685.

⁵ Neumann, *Zeitsch. Elektrochem.*, 1929, 35, 42.

found in the used contact mass, are cited as evidence of its formation as an intermediate compound.¹

Recently a new catalyst has come into use in the form of vanadium pentoxide or a metallic vanadate. A siliceous material of the zeolite type is impregnated with the vanadium compound and ignited; or the catalyst may be mixed with a finely divided porous substance such as kieselguhr or asbestos.² It is claimed that this catalyst is almost as efficient as platinum and possesses the advantage of long life, having great resistance to high temperature and being unaffected by the substances which poison the platinum.³ Neumann⁴ considers that the catalytic action probably depends upon the intermediate formation and reduction of vanadyl sulphate, traces of which are found in the used contact mass.

From a consideration of the details of the ordinary contact process it will readily be recognised that the catalytic method of manufacture of sulphuric acid is capable of yielding an acid of the highest degree of purity.

A promising development in the manufacture of sulphuric acid consists in the combination of the contact and chamber processes, whereby the amount of contact catalyst used is only about one-eighth of that used in the ordinary process.⁵ The gases first pass into a contact chamber and the sulphur trioxide formed is then converted into oleum, whilst unchanged sulphur dioxide passes to the lead chamber to be converted to sulphuric acid. Or, nitrosylsulphuric acid is made to act as a true surface catalyst, intimate contact between it and the gases containing sulphur dioxide and free oxygen being obtained by forcing the gases through fine films of the acid supported on perforated plates, or through a series of tubes containing mixing devices through which the acid circulates; the oxidation proceeds in the liquid phase.

Various other modifications of the sulphuric acid plant are in use, the tendency in recent years being to develop intensive processes in which the reactions leading to the formation of sulphuric acid occur at high velocity.⁶

Physical Properties of Sulphuric Acid.—The "pure" product obtained by evaporation or distillation whether of a dilute or a fuming acid contains as a maximum approximately 98.4 per cent. of H_2SO_4 , the actual figure varying slightly with the pressure.⁷ At extremely low

¹ See also this Series, Vol. IX., Part II., 1925, p. 120.

² Nickell, *Chem. and Met.*, 1928, 35, 153; Alexander, *Chem. and Ind.*, 1929, 48, 871; Spangler, *Ind. Eng. Chem.*, 1929, 21, 417; Jaeger, *ibid.*, 1929, 21, 627; *American Patent*, 1675308 (1928); *British Patent*, 286708 (1928). See also this Series, Vol. VI., Part III., 1929, p. 27.

³ For comparative tests for determining the maximum yields of SO_3 with platinum, vanadium and other catalysts, see Neumann, Panzner and Goebel, *Zeitsch. Elektrochem.*, 1928, 34, 696; Neumann and Goebel, *ibid.*, p. 734; also Jaeger, *loc. cit.*

⁴ Neumann, *ibid.*, 1929, 35, 42.

⁵ *British Patents*, 149648 (1920); 184966, 187016 (1921); 245903 (1925); *German Patents*, 419559, 429835 (1924).

⁶ See further Perley, *Ind. Eng. Chem.*, 1929, 21, 202; *British Patent*, 289879 (1928); Spangler, *Chem. Met. Eng.*, 1928, 35, 342; *Ind. Eng. Chem.*, 1929, 21, 417.

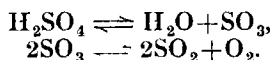
⁷ Bineau, *Ann. Chim. Phys.*, 1848, [iii.], 24, 337; Marignac, *ibid.*, 1853, [iii.], 39, 184; Roscoe, *Trans. Chem. Soc.*, 1860, 13, 146; Pfandl and Polt, *Zeitsch. Chem.*, 1870, 6, 66; Dittmar, *ibid.*, 6, 1; Knietsch, *Ber.*, 1901, 34, 4088; Lunge and Naef, *ibid.*, 1883, 16, 953; Lunge, *ibid.*, 1884, 17, 89; Schertel, *J. prakt. Chem.*, 1882, 26, 246.

pressures evaporation may yield almost pure sulphuric acid.¹ The commercial acid commonly has a concentration of 94 to 97 per cent.

As stated earlier, absolute sulphuric acid of 100 per cent. strength can be obtained as a crystalline solid by fractional crystallisation of the ordinary concentrated acid or by adding the requisite quantity of sulphur trioxide to it; ² the solid has a melting-point of 10.5° C.³ and a latent heat of fusion of 22.82 calories per gram.

Absolute 100 per cent. sulphuric acid when heated begins to boil at 290° C.,⁴ but the temperature rapidly rises to a constant boiling-point of 338° C., when 98.4 per cent. acid distils. This behaviour is due to dissociation ⁵ of the pure acid, which at temperatures above 80° C. is made evident by its fumes, and which can be demonstrated by partial separation of the dissociation products by making use of their unequal rates of diffusion.⁶ The vapour of sulphuric acid is largely dissociated into sulphur trioxide and water; acid above 98.4 per cent. concentration loses trioxide more rapidly than water, whilst acid below this strength parts preferentially with water, the tendency in both cases being for the remaining liquid to attain the concentration of 98.4 per cent., which is that of the acid mixture of minimum vapour pressure.

Vapour density or vapour pressure determinations indicate very considerable dissociation of sulphuric acid vapour into steam and sulphur trioxide at 450° C., and at higher temperatures the dissociation is still further increased, attaining about 50 per cent. at 623° C. under atmospheric pressure.⁷ At these higher temperatures the sulphur trioxide itself suffers partial dissociation (see p. 141):



Near the boiling-point of the acid the vapour density gives indications of a partial association of the sulphuric acid molecules into $(\text{H}_2\text{SO}_4)_x$, where x is probably 2,⁸ in addition to the partial dissociation already mentioned.

Pure sulphuric acid at the ordinary temperature is an odourless, oily liquid; at 0° C. it has a specific gravity of 1.854, at 15° C. 1.8372, and at 21° C., referred to water at the same temperature, 1.834.⁹ The pure

¹ Wanklyn and Robinson, *Proc. Roy. Soc.*, 1863, 12, 507; Stocker and Krafft, *Ber.*, 1906, 39, 2197.

² Domke and Bein (*Zeitsch. anorg. Chem.*, 1904, 43, 125) believe the crystallised acid to fall just short of 100 per cent.

³ Margnac, *loc. cit.*; Mendeléeff and Pawlow, *Ber.*, 1884, 17, 302; Cameron and Macallan, *Proc. Roy. Soc.*, 1889, 46, 13; Thilo, *Chem. Zeit.*, 1893, 16, 1688; Pictet, *Compt. rend.*, 1894, 119, 642; Bronsted, *Zeitsch. physikal. Chem.*, 1910, 68, 693.

⁴ Lunge, *Ber.*, 1878, 11, 373.

⁵ Lunge, *ibid.*, 1884, 18, 89; Aston and Ramsay, *Trans. Chem. Soc.*, 1894, 65, 170.

⁶ Wanklyn and Robinson, *loc. cit.*; Stöcker and Krafft, *loc. cit.*

⁷ Bodenstein and Katayama, *Zeitsch. Elektrochem.*, 1909, 15, 244.

⁸ Vaubel, *J. prakt. Chem.*, 1898, [11], 57, 351; Vernon, *Chem. News*, 1891, 64, 54; Oddo and Anelli, *Gazzetta*, 1911, 41, i., 552.

⁹ Schertel, *J. prakt. Chem.*, 1882, 26, 246; Mendeléeff, *Ber.*, 1884, 17, 302, 2536; 1886, 19, 379; Kohlrausch, *Ann. Phys. Chem.*, 1882, [in.], 17, 82; Lunge and Naef, *loc. cit.*; Richmond, *J. Soc. Chem. Ind.*, 1890, 9, 479; Pictet, *loc. cit.*; Nasini, *Ber.*, 1884, 15, 2885. For the general properties of pure sulphuric acid, especially as a solvent, see Hantzsch, *Zeitsch. physikal. Chem.*, 1907, 61, 257; 1908, 62, 626; 65, 41; 1909, 68, 204; Oddo and Scandola, *ibid.*, 1908, 62, 243; 1909, 66, 138; *Gazzetta*, 1909, 39, ii., 1, 44; 1910, 40, ii., 163.

acid is a very poor conductor of electricity; $\kappa=0.01$ at 25°C . It has a specific heat of 0.835 between 5° and 22°C ., 0.855 between 22° and 80°C ., the value increasing with rise of temperature to 0.870 at 160° to 170°C .² Other physical characteristics include a refractive index, n_D , of 1.42922,³ and a specific inductive capacity of 41.6 at the ordinary temperature.⁴

The gases oxygen, nitrogen and carbon dioxide are dissolved by concentrated sulphuric acid almost to the same extent as by water, but the diluted acid is a poorer solvent in this respect, the minimum solvent power for oxygen and nitrogen occurring with acid mixed with water in the proportions which give maximum contraction on mixing⁵ (see the following). This is not the case, however, with hydrogen chloride; the quantity of this gas absorbed by aqueous solutions of sulphuric acid diminishes with increasing concentration of the latter to a minimum at about 89 per cent. sulphuric acid.⁶

Sulphuric acid is a good solvent for most solids, many organic substances in particular dissolving in it readily;⁷ the molecular weights of substances dissolved in pure sulphuric acid are generally lower than the commonly accepted values, probably due to the formation of dissociable additive compounds between solute and solvent.

Behaviour towards Water.—Water is eagerly absorbed by sulphuric acid, and the concentrated acid is commonly applied as a dehydrating agent for inert gases and organic compounds; with the latter the effect is so marked that compounds containing hydrogen and oxygen, for example the carbohydrates and tartaric acid, are readily carbonised by the acid. The preparation of carbon monoxide from formic acid or oxalic acid is also due to this dehydrating action, but it is remarkable that sulphuric acid of 100 per cent. concentration acts on oxalic acid very slowly in comparison with the slightly diluted acid, the addition of 0.1 per cent. of water increasing the velocity of reaction to seventeen times that observed with the pure acid.⁸

On mixing with water much heat is liberated, 17.7 Calories being liberated per gram-molecule H_2SO_4 if a large excess of water is used; over half this quantity of heat is liberated during the addition of the first two molecular proportions of water. It is uncertain to what extent the evolution of heat is due respectively to hydrate formation and to mere dilution.⁹

As the ordinary heat of formation of sulphuric acid from its elements

¹ Lichty, *J. Amer. Chem. Soc.*, 1908, 30, 1834; Walden, *Zeitsch. anorg. Chem.*, 1902, 29, 371; Biron, *J. Russ. Phys. Chem. Soc.*, 1899, 31, 171; Bouty, *Compt. rend.*, 1889, 108, 393; Kohlrausch, *Ann. Phys. Chem.*, 1876, [ii.], 159, 257.

² Marignac, *Arch. Sci. phys. nat.*, 1870, 30, 217; Pfaundler, *Ber.*, 1870, 3, 738; Biron, *loc. cit.*

³ Nasini, *Ber.*, 1884, 15, 2885; Becquerel, *Ann. Chim. Phys.*, 1877, [v.], 12, 5.

⁴ Weber, *Arch. Sci. phys. nat.*, 1893, [iii.], 29, 571. For the magnetic rotation of polarised light, see Becquerel, *loc. cit.* For the absorption spectrum, see Hartley, *Trans. Chem. Soc.*, 1903, 83, 237.

⁵ Bohr, *Zeitsch. physikal. Chem.*, 1910, 71, 47.

⁶ Cupr, *Publ. Fac. Sci. Univ. Masaryk*, 1925, 63, 1; *Rec. Trav. chim.*, 1925, 44, 476; Coppadoro, *Gazzetta*, 1909, 39, ii., 818.

⁷ Kendall and Carpenter, *J. Amer. Chem. Soc.*, 1914, 36, 2498; also Hantzsch, *loc. cit.*; Oddo and Scandola, *loc. cit.*; Beckmann, *Zeitsch. physikal. Chem.*, 1905, 53, 129; Ateuki and Minaki, *Cellulose Ind. Tokyo*, 1926, 2, 3.

⁸ Bredig and Lichty, *Zeitsch. Elektrochem.*, 1908, 12, 459; Lichty, *J. Physical Chem.*, 1907, 11, 225.

⁹ Kremann and Kerschbaum, *Monatsh.*, 1907, 28, 911.

is 193.0 Calories, the heat of formation from the elements in the presence of a large quantity of water is 210.7 Calories.¹

In contrast to its behaviour with water, sulphuric acid with ice forms freezing mixtures, the temperature falling from 0° C. even to -24° C., the result being still more satisfactory if the acid is previously diluted with a bi- to ter-molecular proportion of water.² The actual absorption of heat is due to the enforced melting of a relatively large quantity of ice.

A mixture of water with sulphuric acid occupies a smaller volume than the two unmixed constituents, considerable contraction being observable (see the following), the maximum effect occurring with 67 to 69 per cent. of acid by weight. With gradual increase in concentration the acid does not exhibit a continuous increase in density, but attains a maximum specific gravity of 1.8442 at 15° C. at a concentration of 97.5 per cent.,³ so that the specific gravity is of little value in testing the acid concentration between 95 and 100 per cent. The following table gives an indication of this abnormal behaviour, the specific gravities being given for the acid at 15° C. compared with water at the same temperature.⁴

Specific Gravity.	Per cent. H ₂ SO ₄ .	Specific Gravity.	Per cent. H ₂ SO ₄ .	Specific Gravity.	Per cent. H ₂ SO ₄ .
1.050	7.82	1.550	64.29	1.825	90.70
1.100	14.29	1.600	68.66	1.830	91.74
1.150	20.90	1.650	72.93	1.835	92.98
1.200	27.21	1.700	77.17	1.840	94.57
1.250	33.81	1.750	81.55	1.844	96.93
1.300	39.18	1.800	86.84	1.8442	97.50
1.350	44.77	1.805	87.5	1.844	98.08
1.400	50.06	1.810	88.20	1.840	99.88
1.450	55.04	1.815	88.95	1.8394	100.00
1.500	59.78	1.820	89.79		

¹ Thomson, *Ber.*, 1870, 3, 46; Berthelot, *Compt. rend.*, 1873, 77, 27; 1877, 85, 651; *Ann. Chim. Phys.*, 1898, [vii.], 13, 77; Rousseau and Tite, *Compt. rend.*, 1891, 113, 191; Pfaunder, *Ber.*, 1870, 3, 799; *Sitzungsber. K. Akad. Wiss. Wien*, 1875, [ii.], 71, 155; Muller, *Bull. Soc. chim.*, 1913, [v.], 13, 1053, 1057; Bose, *Physikal. Zeitsch.*, 1905, 6, 548

² Berthelot, *Compt. rend.*, 1874, 78, 1173.

³ Mendeléeff, *Ber.*, 1886, 19, 387; Bineau, *Ann. Chim. Phys.*, 1848, [iii.], 24, 337; Pickering, *Chem. News*, 1892, 65, 14; Dieterici, *Ann. Phys. Chem.*, 1893, [iii.], 50, 69; Kohlrausch, *Ber.*, 1878, 11, 981; Richmond, *J. Soc. Chem. Ind.*, 1890, 9, 479; Knietzsch, *Ber.*, 1901, 34, 4102. Domke and Bein (*Zeitsch. anorg. Chem.*, 1904, 43, 125) give a maximum density $D_{15}^{15} = 1.8415$ at a concentration of 97.25 per cent.

⁴ Pickering, *Trans. Chem. Soc.*, 1890, 57, 154; Marshall, *J. Soc. Chem. Ind.*, 1899, 18, 4, 1091; 1902, 21, 1508; 1903, 22, 170; Ferguson, *ibid.*, 1905, 24, 781. See also Kolb, *Dyngh. poly. J.*, 1873, 209, 268; Lunge and Naef, *Zeitsch. angew. Chem.*, 1890, 4, 129; Richmond, *J. Soc. Chem. Ind.*, 1890, 9, 479; *Chem. News*, 1894, 69, 236; Mendeléeff, *Ber.*, 1886, 19, 379; Kohlrausch, *Ann. Phys. Chem.*, 1895, [iii.], 56, 198; Loomis, *ibid.*, 1897, [iii.], 60, 547; Rücker, *Phil. Mag.*, 1891, [v.], 32, 304; 1892, 33, 204; Barnes and Scott, *J. Physical Chem.*, 1898, 2, 536. For a specific gravity table for mixtures of sulphuric acid and nitric acid, see Sapozhnikoff, *J. Russ. Phys. Chem. Soc.*, 1905, 37, 374; 1904 26 518

Between 66 and 81 per cent. the relation between the concentration of sulphuric acid and the specific gravity is represented very closely by the formula

$$x = 86S - 69.00,$$

where x is the concentration and S the specific gravity at 15° C. referred to water at the same temperature.¹ The concentration of stronger acid can be determined by diluting with a known proportion of water so that the weakened acid falls somewhere within the stated limits of concentration, then finding the specific gravity.

Another interesting physical method for determining the percentage of sulphuric acid in the concentrated acid is to measure the contraction on mixing with water.² If in a 300 c.c. graduated flask 200 c.c. of the acid under investigation are added to 100 c.c. of water, then after restoring the temperature to 15° C. a contraction is evident; its amount can be measured by the addition of an inert liquid (for example vaseline oil) from a burette to the mixture until the 300 c.c. mark of the flask is reached by the level of the liquid. The contraction with acid of various strengths is as follows:

Percentage of Sulphuric Acid.	Contraction, c.c.	Percentage of Sulphuric Acid.	Contraction, c.c.
98	24.1	91	15.0
97	22.6	90	13.9
96	21.2	89	12.9
95	19.8	88	12.0
94	18.5	87	11.2
93	17.3	86	10.4
92	16.1		

The aqueous vapour pressure of diluted sulphuric acid has been determined over a large range of concentration and temperature.³ The results given in the following table for temperatures up to 90° C. are due to Sorel,⁴ and those from 100° to 200° C. to Briggs.⁵

¹ Marshall, *J. Soc. Chem. Ind.*, 1899, 18, 3.

² Wanklyn and Robinson, *Proc. Roy. Soc.*, 1863, 12, 507. For a table of the proportions of concentrated acid and water necessary to give an acid of any required specific gravity, see Anthon, *J. prakt. Chem.*, 1836, 7, 70.

³ For measurements of the latent heats of vaporisation of aqueous solutions of sulphuric acid, see Vrevski and Nikolski, *J. Russ. Phys. Chem. Soc.*, 1927, 59, 77; of the free energy of dilution, etc., see Randall and Cushman, *J. Amer. Chem. Soc.*, 1918, 40, 393; Smith and Mayer, *ibid.*, 1924, 46, 75; of specific heats of aqueous solutions of various concentrations and of H_2SO_4 - HNO_3 - H_2O mixtures, see Pascal and Garnier, *Bull. Soc. chim.*, 1920, [iv.], 27, 8; of the surface tension of aqueous sulphuric acid of various concentrations, see Livingston, Morgan and Davis, *J. Amer. Chem. Soc.*, 1916, 38, 555; of specific resistivities, see Skowronski and Reinoso, *Trans. Amer. Electrochem. Soc.*, 1927, 51, 113.

⁴ Sorel, *J. Soc. Chem. Ind.*, 1890, 9, 75.

⁵ Briggs, *ibid.*, 1903, 22, 1275. See also Dieterici, *Ann. Phys. Chem.*, 1899, [iii.], 67, 865; Burt, *Chem. News*, 1903, 88, 275; *Trans. Chem. Soc.*, 1904, 85, 1339; Scheel, *Physikal. Zeitsch.*, 1905, 6, 867; Hacker, *Ann. Physik*, 1912, [iv.], 39, 1338; Grollman and Frazer, *J. Amer. Chem. Soc.*, 1925, 47, 712; Greenewalt, *Ind. Eng. Chem.*, 1925, 17, 522; Thomas and Barker, *Trans. Chem. Soc.*, 1925, 127, 2820.

VAPOUR PRESSURE OF AQUEOUS SULPHURIC ACID
(in mm. Hg).

Temperature, ° C.	10	20	30	40	50	60	70	80	90
Concentration H ₂ SO ₄ (per cent.).									
44	4.4	8.5	15.5	28.1	48.3
50	3.3	6.5	12.0	21.4	35.9	61.3	95.6	152.0	236.7
60	1.6	3.0	6.1	10.0	16.9	28.7	46.1	72.3	118.7
70	0.8	1.3	2.5	3.8	5.9	9.5	15.5	25.5	44.4
80	0.2	0.3	0.8	1.3	1.9	2.9	4.1	6.2	9.3

Temperature, ° C.	100	120	140	160	180	200
Concentration H ₂ SO ₄ (per cent.).						
77.51	20.2	71.0	168.5
81.81	8.5	32.5	75.7	207.5
87.32	2.4	8.7	26.3	63.8	132.5	367
91.22	10.0	25.0	62	149

Hydrates of Sulphuric Acid.—The avidity of sulphuric acid for water naturally suggests the possible formation of definite compounds or hydrates, and the existence of such hydrates has been demonstrated in various ways.

The freezing-point curve for mixtures of two substances is usually regarded as affording definite evidence of the occurrence or otherwise of chemical combination between the constituents, and with mixtures of sulphuric acid and water very definite results are obtained.¹ With sulphur trioxide and water as the two components, maxima on the freezing-point curve (fig. 12) occur at proportions corresponding with the compositions of the following compounds: SO₃, H₂S₂O₇, H₂SO₄, H₂SO₄.H₂O, H₂SO₄.2H₂O, H₂SO₄.4H₂O, H₂O. Thus the existence of a mono-, a di- and a tetra-hydrate of sulphuric acid in the solid condition is proved, but the possibility of other hydrates, for instance H₂SO₄.3H₂O, 3H₂SO₄.H₂O and H₂SO₄.12H₂O, under other conditions, is not excluded. The final portion of the curve towards 100 per cent. SO₃ is uncertain owing to the nature of sulphur trioxide (p. 139), and is therefore not included in the figure.

Other indications of the existence of hydrates are found in the curve representing the electrical conductivity of solutions of various

¹ Pickering, *Trans. Chem. Soc.*, 1890, 57, 331; *Ber.*, 1892, 25, 1099; see also *Chem. News*, 1889, 59, 248; *Zeitsch. physikal. Chem.*, 1891, 7, 378; Giran, *Compt. rend.*, 1913, 157, 221; Knietsch, *Ber.*, 1901, 34, 4100; Biron, *J. Russ. Phys. Chem. Soc.*, 1899, 31, 517; Pictet, *Compt. rend.*, 1894, 119, 642; Thilo, *Chem. Zeit.*, 1892, 16, 1688.

concentrations, minima occurring at the compositions SO_3 , H_2SO_4 , $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$; ¹ also in the refractive index curve ² a maximum is found at the proportion $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, whilst sharp breaks occur at H_2SO_4 , $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$. The viscosity curve ³ also indicates a series of compounds SO_3 , $\text{H}_2\text{S}_2\text{O}_7$, H_2SO_4 , $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, H_2O , whilst the thermal expansion of sulphuric acid of various concentrations gives indications of the hydrates $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$.⁴ Particularly clear evidence of hydrate formation is available from determinations of the molecular weight of various mixtures of sulphuric acid and water, using acetic acid as cryoscopic solvent,⁵ the results demonstrating the

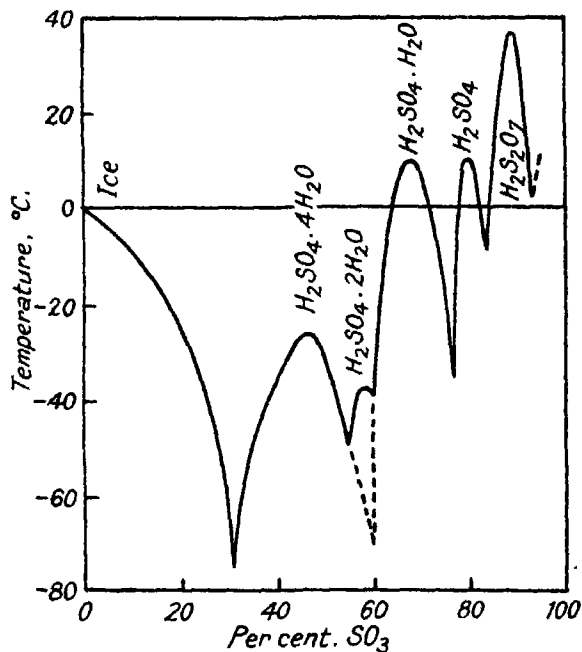


FIG. 12.—Freezing-point Curve for $\text{SO}_3\text{-H}_2\text{O}$.

occurrence of $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, and also the probability of a higher hydrate, $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, and a lower one, $2\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

The relation between specific gravity and concentration gives no definite confirmation of the presence of hydrates in diluted sulphuric acid.⁶

¹ Kohlrausch, *Ann. Phys. Chem.*, 1885, [iii.], 26, 161; 1882, [iii.], 17, 69; Crompton, *Trans. Chem. Soc.*, 1888, 53, 116.

² Pickering, *Trans. Chem. Soc.*, 1893, 63, 99; Féry, *Compt. rend.*, 1892, 115, 1309; Kohlrausch and Hallwachs, *Ann. Phys. Chem.*, 1894, [iii.], 53, 14; Le Blanc, *Zeitsch. physikal. Chem.*, 1895, 67, 1838; Veley and Manley, *Proc. Roy. Soc.*, 1905, [A], 76, 469.

³ Dunstan and Wilson, *Trans. Chem. Soc.*, 1907, 91, 83; 1908, 93, 2179; Dunstan, *Proc. Chem. Soc.*, 1914, p. 104; Knietzsch, *Ber.*, 1901, 34, 4069.

⁴ Domke and Bein, *Zeitsch. anorg. Chem.*, 1905, 43, 125; Mendeléeff, *Ber.*, 1886, 19, 380.

⁵ Jones, *Amer. Chem. J.*, 1894, 16, 1; *Zeitsch. physikal. Chem.*, 1894, 13, 419.

⁶ Pickering, *loc. cit.*; Mendelejew, *Zeitsch. physikal. Chem.*, 1887, 1, 275. For other investigations bearing on this subject, see Thomsen, *Ber.*, 1870, 3, 496; Perkin, *Trans. Chem. Soc.*, 1886, 49, 777; Berthelot, *Compt. rend.*, 1874, 78, 716; Schneider, *Monatsh.*, 1890, 11, 116. A summary of various methods and the corresponding results is given by Morgan and Davis, *J. Amer. Chem. Soc.*, 1916, 38, 555.

Sulphuric acid monohydrate,¹ $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, crystallises from acid of the corresponding concentration in hexagonal prisms which melt at $+9^\circ \text{C}$.; the *dihydrate*, $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, melts at -37°C ., and the *tetrahydrate*, $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, at -24.5°C . These hydrates are relatively unstable and in the molten condition are dissociated to a considerable extent, behaving as ordinary dilute sulphuric acid. As is indicated in fig. 12, the melting-points of these hydrates are lowered very considerably by the presence of a slight excess of either constituent.

It is worthy of note that the physical properties of mixtures of sulphuric acid and ethyl ether also indicate the formation of additive compounds,² for example $\text{H}_2\text{SO}_4 \cdot (\text{C}_2\text{H}_5)_2\text{O}$, in which the ether may be regarded as functioning in the same manner as does the molecule of water in the hydrate $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. Ethyl alcohol, which is analogous in many ways to water, behaves in a different manner³ with sulphuric acid, giving ethyl hydrogen sulphate, $(\text{C}_2\text{H}_5)\text{HSO}_4$, and other products.

Ionisation of Sulphuric Acid.—In aqueous solution sulphuric acid undergoes electrolytic dissociation with formation of H^+ and HSO_4' ions, the latter dissociating in part still further into H^+ and SO_4'' ions, especially if the solution is dilute. Examination by the various available physico-chemical methods shows that, regarded from the point of view of the first stage of dissociation or, in other words, considering the acid as monobasic, sulphuric acid is comparable in strength (as distinct from concentration) with hydrochloric and nitric acids; the second stage, $\text{HSO}_4' \rightleftharpoons \text{H}^+ + \text{SO}_4''$, however, has much less tendency to proceed to completion, and, in consequence of this, sulphuric acid, acting as a dibasic acid, is considerably inferior in strength to nitric acid and the halogen hydracids, excluding hydrofluoric acid.⁴ Its ability to displace these acids completely from their salts is dependent on its lower volatility.

Electrolysis.—On electrolysis of acid below 20 per cent. concentration the products are mainly hydrogen and oxygen (with ozone),⁵ but with more concentrated acid the conversion of HSO_4' ions at the anode into free HSO_4 groups is succeeded by the coupling of the latter to form molecules of perdisulphuric acid, $\text{H}_2\text{S}_2\text{O}_8$,⁶ which changes more or less

¹ Care is necessary to avoid confusion in terminology with these hydrates because, unfortunately, pure sulphuric acid, H_2SO_4 , is frequently but incorrectly termed "sulphuric acid monohydrate."

² Archibald and McIntosh, *Trans. Chem. Soc.*, 1904, 85, 919; Tschelnzef and Kozlov, *J. Russ. Phys. Chem. Soc.*, 1914, 46, 408; Pound, *Trans. Chem. Soc.*, 1911, 99, 698.

³ For instance, see Kremann, *Monatsh.*, 1910, 31, 245, 671, 1051; Villiers, *Compt. rend.*, 1903, 136, 1452.

⁴ Traube, *Ber.*, 1892, 9, 487; Trevor, *Zeitsch. physikal. Chem.*, 1892, 10, 335; Jones, *ibid.*, 1893, 12, 628; Kay, *Proc. Roy. Soc. Edin.*, 1898, 22, 493; Whetham, *Proc. Roy. Soc.*, 1900, 66, 192; 1905, [A], 76, 577; 1908, [A], 81, 58; Jones and Murray, *Amer. Chem. J.*, 1903, 30, 205; Felipe, *Physikal. Zeitsch.*, 1905, 6, 422; Luther, *Zeitsch. Elektrochem.*, 1907, 13, 294; Huybrechts, *Ann. Chim. Phys.*, 1907, [viii.], 11, 68; Jahn, *Zeitsch. physikal. Chem.*, 1907, 58, 641; Kato, *Mem. Col. Sci. Eng. Kyōtō*, 1908, i, 332; Noyes and Stewart, *J. Amer. Chem. Soc.*, 1910, 32, 1133; Kremann and Brassert, *Monatsh.*, 1910, 31, 195; Enklaar, *Chem. Weekblad*, 1911, 8, 824; 1912, 9, 28; Richardson and Taylor, *Trans. Amer. Electrochem. Soc.*, 1911, 20, 179; Drucker, *Zeitsch. Elektrochem.*, 1911, 17, 398; *Zeitsch. physikal. Chem.*, 1912, 80, 630; Tolman and Greathouse, *J. Amer. Chem. Soc.*, 1912, 34, 364; Ferguson and France, *ibid.*, 1921, 43, 2150, 2161; Kolthoff, *Rec. Trav. chim.*, 1924, 43, 207.

⁵ Geuther, *Annalen*, 1859, 109, 129; Gladstone and Tribe, *Ber.*, 1879, 12, 389; *Trans. Chem. Soc.*, 1883, 43, 344; McLeod, *ibid.*, 1886, 49, 591.

⁶ Berthelot, *Compt. rend.*, 1878, 86, 20, 71, 277; 1880, 90, 269, 331; 1891, 112, 1481; *Ann. Chim. Phys.*, 1892, [vi.], 26, 826; Marshall, *Trans. Chem. Soc.*, 1891, 59, 771; Elbs

rapidly according to the concentration into permonosulphuric acid, H_2SO_5 ; ¹ this last product, again, can undergo further change, giving rise to hydrogen peroxide.

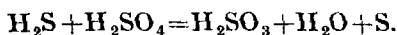
Sulphuric acid of 98 per cent. strength undergoes decomposition on electrolysis. At 50° C. hydrogen, hydrogen sulphide and sulphur are liberated at the cathode; at higher temperatures the cathodic products are sulphur dioxide and sulphur, until at 300° C. only sulphur is liberated. Up to 200° C. oxygen alone is evolved at the anode, but with rise in temperature sulphur dioxide also appears, resulting from oxidation of sulphur which has diffused from the cathode chamber; above 280° C. the two gases leave the anode in quantities in accordance with Faraday's Law.²

Chemical Properties of Sulphuric Acid.—Concentrated sulphuric acid possesses marked oxidising power, especially in the presence of certain metallic salts, such as those of mercury and copper. Gaseous hydrogen begins to undergo appreciable oxidation by sulphuric acid at 160° C.,³ but nascent hydrogen or hydrogen in contact with finely divided platinum can effect the reduction of the acid even at the ordinary temperature.⁴ If a mixture of hydrogen and sulphuric acid vapour is passed over silica heated at 700° to 900° C., quantitative reduction to hydrogen sulphide occurs.⁵ The acid slowly oxidises carbon to carbon dioxide,⁶ this process occurring in the Kjeldahl process for the estimation of nitrogen in organic substances. The reaction with carbon monoxide proceeds according to the equation



as long as the acid concentration does not fall below 91 per cent.; ⁷ certain catalysts, *e.g.* mercury, silver, selenium, palladium and iridium, but not platinum or osmium, accelerate this reaction. Phosphorus is oxidised to phosphoric acid by sulphuric acid,⁸ and sulphur to sulphur dioxide, in both cases the assistance of heat being necessary.

Hydrogen sulphide reacts with concentrated solutions of sulphuric acid yielding sulphur and sulphurous acid, thus :



At the ordinary temperature the concentration of the acid must not be much less than 25*N* for separation of sulphur to occur. It has been suggested, therefore, that it is really pyrosulphuric acid, $\text{H}_2\text{S}_2\text{O}_7$, which reacts with the hydrogen sulphide, this acid being present in small equilibrium quantity in the concentrated acid solution. The first stage of the reaction would thus be :

and Schonherr, *Zeitsch. Elektrochem.*, 1895, 1, 417, 468; 2, 245; Elbs, *Zeitsch. angew. Chem.*, 1897, p. 195.

¹ Caro, *Zeitsch. angew. Chem.*, 1898, p. 845; Traube, *Ber.*, 1889, 22, 1518; 1891, 24, 1764; 1892, 25, 95; Baeyer and Villiger, *ibid.*, 1901, 34, 853.

² Hoffmann, *Zeitsch. Elektrochem.*, 1921, 27, 442. For the effect of an alternating current on sulphuric acid, see Lattey, *Phil. Mag.*, 1925, [vi.], 50, 444.

³ Warner, *Chem. News*, 1873, 28, 13; Berthelot, *Compt. rend.*, 1897, 125, 743; *Ann. Chim. Phys.*, 1898, [vii.], 13, 64; Milbauer, *Zeitsch. physikal. Chem.*, 1907, 57, 649; 1911, 77, 380. Cf. Jones, *Mem. Manchester Phil. Soc.*, 1917, 61, No. 3, 1-3.

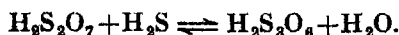
⁴ Cooke, *Chem. News*, 1888, 58, 103; Pomilio, *Rend. Accad. Sci. Fis. Mat. Napoli*, 1915, [iii.], 21, 19.

⁵ Vila, *Compt. rend.*, 1924, 179, 1163.

⁶ Berthelot, *Ann. Chim. Phys.*, 1898, [vii.], 14, 206; Philippi and Seka, *Monatsh.*, 1927, 48, 375.

⁷ Milbauer, *Chem. Zeit.*, 1918, 42, 313.

⁸ Oppenheim, *Bull. Soc. chim.*, 1864, [ii.], 1, 163.



The trithionic acid would then decompose as indicated on p. 212, ultimately yielding sulphurous acid and sulphur.¹

Hydrobromic acid reduces sulphuric acid to sulphur dioxide, as also does hydriodic acid, but with the latter in high concentration the reduction goes further, producing sulphur and hydrogen sulphide.² For this reason when metallic bromides and iodides are treated with sulphuric acid, the halogen element is liberated, the temperature at which this becomes evident depending on the concentration of the acid; thus, with the potassium salts, the following observations have been made.³

Concentration of acid, per cent. H_2SO_4	25	30	35	40	50
Temperature, ° C., at which I_2 detected	100	60	50	45	36
Concentration of acid, per cent. H_2SO_4	60	70	80	90	..
Temperature, ° C., at which Br_2 detected	169	100	46	38	..

Stannous chloride also causes reduction to hydrogen sulphide.⁴

Sulphuric acid is oxidised to permonosulphuric, perdisulphuric and fluorosulphuric acids when an ice-cold aqueous solution is treated with fluorine. In addition to the foregoing products, ozone and a very unstable compound believed to be a tetroxide (SO_4 or S_2O_8) are also produced.⁵ A similar oxidation occurs when fluorine is passed into cold solutions of alkali sulphates or hydrogen sulphates.

Sodium and potassium attack the pure acid even in the cold, the action with hot acid being explosive.⁶ Other metals, for example iron, zinc, magnesium and manganese, which liberate hydrogen readily from hydrochloric acid, behave similarly with dilute sulphuric acid, but with the concentrated acid the reaction is more sluggish, generally requiring to be aided by heat, and, as any hydrogen which might be produced becomes oxidised by the acid, the gaseous product is sulphur dioxide.⁷ Silver, lead, mercury and copper are attacked only by the hot concentrated acid;⁸ by-reactions frequently occur, such as the formation of

¹ Bassett and Durrant, *J. Chem. Soc.*, 1927, p. 1420.

² *ibid.*, 1891, 24, 451; Bush, *J. Physical Chem.*, 1929, 33, 613.

³ *ibid.*, 1929, 33, 717.

⁴ *ibid.*, 1896, 18, 251.

⁵ Fichter and others, *Helv. Chim. Acta*, 1926, 9, 602; 1927, 10, 553.

⁶ Ditte, *Ann. Chim. Phys.*, 1890, [vi.], 19, 68; Burch and Dodgson, *Chem. News*, 1894, 69, 225.

⁷ Berthelot, *Ann. Chim. Phys.*, 1898, [vii.], 14, 176; Knietzsch, *Ber.*, 1901, 31, 4109; Ditte, *loc. cit.*; Kolbe, *Dingl. poly. J.*, 1861, 162, 77; Mur, *Chem. News*, 1881, 44, 237; 1887, 56, 205; *Trans. Chem. Soc.*, 1888, 53, 47; Mur and Robbs, *Chem. News*, 1882, 45, 70; Pullinger, *Trans. Chem. Soc.*, 1890, 57, 815; Adie, *Proc. Chem. Soc.*, 1899, 15, 132; Fawsitt and Pain, *J. Proc. Roy. Soc. N.S. Wales*, 1918, 52, 396; Fawsitt, *J. Soc. Chem. Ind.*, 1920, 39, 147.

⁸ Fordos and Gélis, *J. Pharm. Chim.*, 1841, 27, 730; Calvert and Johnson, *Compt. rend.*, 1863, 56, 140; Hasenclever, *Chem. News*, 1872, 26, 174; Mallard, *Bull. Soc. chim.*, 1874,

some metallic sulphide due to reduction of sulphate, and in the case of copper not only are cupric sulphate and cuprous sulphide commonly obtained,¹ but cuprous sulphate may also be found in solution;² indeed, the reaction, if carried out at about 200° C., provides a means of preparing the last-named salt.³ Platinum is attacked very appreciably by sulphuric acid at 250° C., the effect being diminished by the presence of reducing agents such as carbon, sulphur, sulphur dioxide or arsenious oxide.⁴

The interaction of a mixture of nitric oxide and nitrogen dioxide with sulphuric acid has already been referred to (p. 153); nitric oxide alone is only slightly absorbed by the pure acid and not appreciably by the somewhat diluted acid such as is used in the nitrometer.⁵

Mention has been made already of the action of phosphorus pentachloride on sulphuric acid (p. 98).⁶

Applications of Sulphuric Acid.⁷—In addition to various purposes already mentioned, sulphuric acid is applied on an immense scale in the inorganic chemical industry for the manufacture of acids such as hydrochloric, nitric, hydrofluoric and phosphoric acids, and directly or indirectly in the production of many other chemical substances such as phosphorus, chlorine, bromine, iodine, sodium carbonate, hydrogen peroxide and, of course, sulphates. The "superphosphate of lime" industry, by which ordinary insoluble calcium phosphate is converted into a form which can act as a fertiliser, supplying phosphorus in a condition suitable for absorption by the roots of plants, consumes immense quantities of sulphuric acid, as also does the production of ammonium sulphate in coke ovens and gas works. Much sulphuric acid is also used in electric batteries of various types, accumulator cells in particular requiring a dilute acid of a high degree of purity. Metallurgical industry also calls for large quantities of sulphuric acid, especially for use in "pickling" metals, i.e. cleansing metallic surfaces from

22, 114; Napier and Tatlock, *Chem. News*, 1880, 42, 314; *Ber.*, 1881, 14, 121; Glover, *Chem. News*, 1882, 45, 105; Cookson, *ibid.*, 1882, 45, 106; Mactear, *ibid.*, 1880, 41, 236; Pitkin, *Trans. Chem. Soc.*, 1885, 48, 460; Lunge and Schmid, *Zeitsch. angew. Chem.*, 1892, p. 642; Knetsch, *loc. cit.*; Baskerville and Miller, *Chem. News*, 1898, 77, 191; Pitman, *J. Amer. Chem. Soc.*, 1898, 20, 100; Berthelot, *Compt. rend.*, 1897, 125, 749.

¹ Barruel, *J. Pharm. Chim.*, 1834, 20, 13; Calvert and Johnson, *Trans. Chem. Soc.*, 1866, 19, 438; Pickering, *ibid.*, 1878, 33, 113; Baskerville, *J. Amer. Chem. Soc.*, 1895, 17, 904; 1896, 18, 942; Baskerville and Miller, *ibid.*, 1897, 19, 1873; Andrews, *Amer. Chem. J.*, 1896, 18, 251.

² Scheurer-Kestner, *Dingl. poly J.*, 1876, 221, 82; *Compt. rend.*, 1880, 191, 59; Pickering, *Trans. Chem. Soc.*, 1878, 33, 112; Margules, *Ann. Phys. Chem.*, 1898, (3), 65, 629; 66, 540; Baskerville, *J. Amer. Chem. Soc.*, 1896, 17, 90; 18, 942; Andrews, *ibid.*, 18, 251; Adie, *Chem. News*, 1899, 77, 261; Conroy, *J. Soc. Chem. Ind.*, 1903, 22, 465; Ruer, *Zeitsch. Elektrochem.*, 1903, 9, 235; Brochet and Petit, *ibid.*, 1904, 10, 909; *Compt. rend.*, 1905, 140, 655; Delépine, *ibid.*, 1906, 142, 631; Cundall, *Trans. Chem. Soc.*, 1914, 105, 60; Rogers, *ibid.*, 1926, p. 253; Druce, *Chem. News*, 1928, 136, 81; Fowles, *ibid.*, 136, 257.

³ See Druce and Fowles, *ibid.*, 137, 385.

⁴ For the behaviour of other metals towards sulphuric acid, see Smith, *J. Soc. Chem. Ind.*, 1904, 23, 475, (Al); Nissenson and Crocogino, *Chem. Zeit.*, 1902, 26, 984, also Muir and Robbs, *Chem. News*, 1882, 45, 69, (Sn and Sb).

⁵ Lunge, *J. Soc. Chem. Ind.*, 1885, 4, 447; *Ber.*, 1886, 19, 111; Nettlefold, *Chem. News*, 1887, 55, 28. See also Allen, *J. Soc. Chem. Ind.*, 1885, 4, 178; Bayley, *Chem. News*, 1886, 53, 6.

⁶ For the chemical behaviour of sulphuric acid at low temperatures, see Franklin and Kraus, *Amer. Chem. J.*, 1900, 20, 820; Pictet, *Compt. rend.*, 1892, 115, 816.

⁷ See *Chemische Technologie*, vol. i. (1895), and *Chemische Technologie der Neuzeit*, vol. i. (1905), by Dammer.

rust and dirt; thus, in South Wales, steel plate is almost exclusively pickled with sulphuric acid before tinning.

The organic chemical industry likewise consumes much sulphuric acid for a wide variety of purposes. The acid is not only used for the preparation of sulphonc acids, a process of particular importance in the coal tar dye industry, but is also applied as an oxidising agent, for example in the production of phthalic anhydride from naphthalene, which is also an important step in the manufacture of various dyes such as indigo and eosin; in applying the sulphuric acid for sulphonation or for oxidation purposes, traces of mercury compounds frequently exert a marked catalytic influence. Sulphuric acid is also used in the purification of various kinds of oils, especially mineral oils, and directly or indirectly in the hydrolytic decomposition of various animal and vegetable oils and fats for the production of glycerine and fatty acids, the latter being further convertible into soap and candles. The conversion of paper into "vegetable parchment," of viscose into artificial silk, and of starch into glucose for various purposes, are also processes involving sulphuric acid. Together with nitric acid, sulphuric acid is applied to the production of many organic nitro-compounds, for example nitrobenzene, dinitrobenzene, picric acid and the various nitrotoluenes, which are of importance for the manufacture of dyes and explosives, and of certain organic nitrates, in particular the misnamed nitrocellulose and nitroglycerine, which should more correctly be termed cellulose nitrate and glyceryl nitrate.

The use of weak solutions of sulphuric acid (1 to 2 per cent.) as a weed spray has been suggested.¹

The Sulphates.—Various methods for the formation of the salts of sulphuric acid will be found under the heading of the properties of the acid, of its anhydride and of sulphur dioxide; further details may be found under the description of the sulphates themselves in the other volumes of this series.

The *normal sulphates* usually form well-defined crystals containing water of crystallisation, and frequently exhibit isomorphism not only with one another² but in some cases also with the corresponding selenates, tellurates and chromates. They are generally fairly soluble in water, the chief exceptions being the sulphates of barium,³ strontium and lead, which are commonly classed as "insoluble," and of calcium and silver, which are sparingly soluble.⁴

Acid salts of the type XHSO_4 , where X represents the equivalent weight of a metal, are also known, the hydrogen sulphates or "bisulphates" of the alkali metals being the commonest examples.⁴ These

¹ Aslander, *J. Agric. Res.*, 1927, 34, 1065.

² See, e.g., Retgers, *Zeitsch. physikal. Chem.*, 1891, 8, 24; Tutton, *Zeitsch. Kryst. Min.*, 1894, 28, 131; *Trans. Chem. Soc.*, 1896, 69, 344; Wyruboff, *Bull. Soc. chim.*, 1889, [iii.], 2, 501; Arzrum, *Zeitsch. Kryst. Min.*, 1877, 1, 165.

³ To obtain colloidal solutions of barium sulphate, see Lott, *J. Amer. Pharm. Assoc.*, 1928, 17, 454.

⁴ Schultz, *Ann. Phys. Chem.*, 1870, [ii.], 139, 480. See also Stortenbeker, *Rec. Trav. chim.*, 1902, 21, 399; Recoura, *Compt. rend.*, 1903, 137, 118, 189; Colson, *ibid.*, 1903, 136, 366; Hollard, *Bull. Soc. chim.*, 1906, [iii.], 35, 1240; d'Ans and others, *Ber.*, 1906, 39, 1534; *Zeitsch. anorg. Chem.*, 1907, 53, 149; 1909, 61, 91; 63, 225, 228, 231; Holmes, *Trans. Chem. Soc.*, 1907, 91, 1606; Arzhar, *Compt. rend.*, 1908, 147, 129; Berguis, *Zeitsch. physikal. Chem.*, 1910, 72, 338; van Dorp, *ibid.*, 1913, 86, 109; 1910, 73, 284; Pascal and Ero, *Bull. Soc. chim.*, 1919, [iv.], 25, 35; Dominik, *Przemysl Chem.*, 1921, 5, 10, 37, 631.

give acidic aqueous solutions, due to partial conversion into the corresponding normal sulphate and sulphuric acid, or in other words, to the further electrolytic dissociation of the HSO_4' ions. Under suitable conditions acid sulphates containing additional molecules of sulphuric acid¹ can be obtained; for example, the following exist: $\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{SO}_4$, $2\text{Na}_2\text{SO}_4 \cdot 9\text{H}_2\text{SO}_4$, $\text{K}_2\text{SO}_4 \cdot 8\text{H}_2\text{SO}_4$, $\text{BaSO}_4 \cdot 2\text{H}_2\text{SO}_4$. Viscosity measurements of aqueous solutions of normal ammonium sulphate, sulphuric acid, and ammonium hydrogen sulphate, indicate that the formation of the acid salt is accompanied by an increase of internal friction.² The appreciable solubility of the sulphates of lead,³ barium⁴ and strontium in concentrated sulphuric acid probably is also due to the formation of acid salts, which on dilution of the acid undergo decomposition into sulphuric acid and the original insoluble sulphate. When heated, the alkali hydrogen sulphates undergo dehydration into the corresponding pyrosulphates, further heating then causing decomposition into normal sulphate and sulphur trioxide (see p. 147); the hydrogen sulphates of the other metals yield normal sulphates directly.

Basic sulphates are obtained when the normal sulphates of antimony, bismuth and mercury are treated with water, sulphuric acid being produced simultaneously. These salts are insoluble in water. Many other metals, for example copper,⁵ aluminium⁶ and tin,⁷ yield precipitates of basic sulphates on the addition of alkali to aqueous solutions of their normal sulphates.

The normal sulphates show a marked tendency to the formation of *double salts*,⁸ the best known case being that of the *alums*, which are isomorphous compounds of the general formula $\text{M}_2(\text{SO}_4)_3 \cdot \text{X}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, where M and X represent a trivalent and univalent metal, respectively; in aqueous solution these double salts are almost entirely resolved into the ions of their constituent salts,⁹ recombination taking place as the solution crystallises. Double salts are also formed by the crystallisation of fused mixtures of anhydrous sulphates, the freezing-point curves supplying evidence of the occurrence of combination between the constituents.¹⁰

Certain halogen salts appear to be isomorphous with potassium sulphate and able to form "alums" with aluminium sulphate; thus,

¹ Kendall and Landon, *J. Amer. Chem. Soc.*, 1920, 42, 2131; Kendall and Davidson, *ibid.*, 1921, 43, 979; Cambi and Bozza, *Ann. Chim. appl.*, 1923, 13, 221.

² Grunert, *Zeitsch. anorg. Chem.*, 1925, 145, 394.

³ Ditz and Kanhauser, *Zeitsch. anorg. Chem.*, 1916, 98, 128; Dawkins and Weldon, *Proc. Soc. Chem. Ind. Victoria*, 1922, 22, 940.

⁴ Meyer and Friedrich, *Zeitsch. physikal. Chem.*, 1922, 101, 498.

⁵ Williamson, *J. Physical Chem.*, 1923, 27, 789; Kruger, *J. prakt. Chem.*, 1924, [ii], 108, 278.

⁶ Williamson, *J. Physical Chem.*, 1923, 27, 284.

⁷ Carson, *J. Amer. Chem. Soc.*, 1926, 48, 906.

⁸ See, e.g., Étard, *Compt. rend.*, 1878, 86, 1399; 87, 602; Ber., 1879, 12, 360; Scott, *Trans. Chem. Soc.*, 1897, 71, 564; Barre, *Compt. rend.*, 1909, 149, 292; Palache and Warren, *Amer. J. Sci.*, 1908, [iv.], 26, 342; Zambonini and Carobbi, *Atti R. Accad. Lincei*, 1924, [v.], 33, 301.

⁹ Favre and Valson, *Compt. rend.*, 1873, 77, 909; Rudorff, *Ber.*, 1882, 15, 3044; Linebarger, *Amer. Chem. J.*, 1893, 15, 337; Wyckoff, *Amer. J. Sci.*, 1923, 5, 209; Müller, *Zeitsch. physikal. Chem.*, 1924, 112, 161.

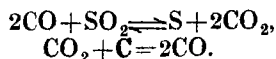
¹⁰ Mallet, *Chem. News*, 1899, 80, 300; *Trans. Chem. Soc.*, 1900, 77, 216; 1902, 81, 1548; Calcagni and others, *Gazzetta*, 1913, 43, ii., 380; *Atti R. Accad. Lincei*, 1910, [v.], 19, ii., 242; 1912, [iv.], 21, i., 483; 1912, [v.], 21, ii., 71, 93; 1913, [v.], 22, ii., 373.

the salts $K_2BeF_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ and $K_2ZnCl_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ are "alums," crystallising in the cubic system, normally as octahedra.¹

All sulphates undergo reduction when heated with carbon, the product being the metal, metallic sulphide or metallic carbide, according to the salt in question and the conditions of the treatment.² Magnesium sulphate, however, when heated with carbon at 750° C., yields the oxide and free sulphur, the primary reaction being³



sulphur being liberated according to the reversible secondary reaction :



Magnesium reduces anhydrous sulphates with vigour at high temperatures.⁴ Reduction to sulphide may be brought about by certain micro-organisms in the presence of animal fats, the latter being anaerobically decomposed during the process.⁵

Although sulphuric acid expels many other acids from their salts, it can in a similar manner be displaced from its own salts by heating with still less volatile acids such as phosphoric or boric acid or even with silica or alumina ;⁶ on account of the high temperature necessary, the liberated sulphuric acid or anhydride is partly decomposed into sulphur dioxide.

At very high temperatures the sulphates of metals such as copper, zinc, iron, aluminium and chromium tend to lose sulphur trioxide (largely in the form of sulphur dioxide and oxygen) and to give residues of the corresponding oxides.⁷ Calcium sulphate is stable up to 1300° C., above which temperature it melts and immediately undergoes almost complete decomposition with abundant evolution of fumes.⁸ Very slight decomposition has been observed with barium sulphate at 1300° C.⁹

Additive compounds of the type $MSO_4 \cdot 2HCl$ are formed by the sulphates of those metals the chlorides of which do not readily yield hydrogen chloride when treated with sulphuric acid.¹⁰ Thus such compounds of cadmium, copper, lead, mercury, silver, thallium and tin have been prepared ; the hydrogen chloride may be expelled by heat.

Molecular Weight and Constitution of Sulphuric Acid.—Allowing for the effect of electrolytic dissociation, the behaviour of sulphuric acid in aqueous solution is consistent with the formula H_2SO_4 . In the vapour state also, allowance being made for gaseous dissociation, the

¹ Curjel, *Nature*, 1929, 123, 206.

² E.g. see Mourlot, *Ann. Chim. Phys.*, 1899, [vi.], 17, 510 ; Riesenfeld, *J. prakt. Chem.*, 1920, [ii.], 100, 115.

³ Althammer, *Kali*, 1924, 18, 112.

⁴ Brückner, *Monatsh.*, 1905, 26, 675.

⁵ Seliber, *Compt. rend. Soc. Biol.*, 1928, 99, 544 ; *Chem. Zentr.*, 1928, ii., 1781.

⁶ Marchal, *Compt. rend.*, 1929, 188, 258, 399.

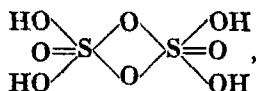
⁷ Wöhler, Plüddemann and Wöhler, *Ber.*, 1908, 41, 703 ; Keppeler and d'Ans, *Zeitsch. physikal. Chem.*, 1908, 62, 89 ; O'Sullivan, *Analyst*, 1914, 39, 425 ; Hofman and Wanjukow, *Zeitsch. Kryst. Min.*, 1915, 55, 111.

⁸ Budnikov and Syrkín, *Chem. Zeit.*, 1923, 47, 22.

⁹ Marchal, *Bull. Soc. chim.*, 1929, [iv.], 45, 339.

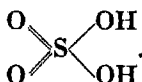
¹⁰ Ephraim, *Ber.*, 1925, 58, [B], 2262 ; 1926, 59, [B], 790.

molecular weight agrees fairly well with this formula, except that at temperatures in the neighbourhood of the boiling-point there is distinct evidence of partial association into double molecules (see p. 168). In the liquid state it is probable that the pure acid is associated into larger molecules, the low vapour pressure and the surface tension¹ supplying evidence in favour of a higher molecular weight than H_2SO_4 , which receives confirmation from the ready formation of double sulphates. It may be assumed that formation of the larger molecules occurs by the oxygen atoms acting as links, as expressed in the bimolecular formula



which is analogous with the formula already proposed (p. 144) for dimeric sulphur trioxide.

In accordance with the dualistic views of earlier days, the composition of sulphuric acid was at one time expressed by the formula $\text{H}_2\text{O}.\text{SO}_3$, but to-day the formula $\text{SO}_2(\text{OH})_2$ is generally adopted, commonly with the assumption of sexavalent sulphur, so that the structural formula is



The presence of the two hydroxyl groups in the molecule is shown by the action of chlorine and of phosphorus pentachloride, which respectively produce chlorosulphonic acid, HSO_3Cl (p. 97), and pyrosulphuryl chloride, $\text{S}_2\text{O}_5\text{Cl}_2$ (p. 95). Moreover, both these products with water yield sulphuric and hydrochloric acids. Since the alkali alkylsulphates, for example $\text{C}_2\text{H}_5\text{O}.\text{SO}_2.\text{OK}$, do not exist in two isomeric forms, it is evident that the two hydroxyl groups are symmetrically placed in the molecule. That the hydroxyl groups are directly attached to the sulphur atom may be deduced from such transformations as the following: Concentrated sulphuric acid reacts directly with benzene on heating to produce benzenesulphonic acid; this with phosphorus pentachloride yields the corresponding chloride, which on reduction gives thiophenol,



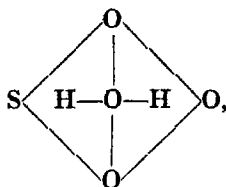
The latter compound on oxidation again yields the sulphonic acid. Again, sulphuryl chloride reacts with benzene in the presence of aluminium chloride to give diphenylsulphone, $(\text{C}_6\text{H}_5)_2\text{SO}_2$, a compound which can also be obtained by oxidation of diphenyl sulphide, $(\text{C}_6\text{H}_5)_2\text{S}$. On the assumption that the phenyl radicals remain attached to the sulphur atom throughout these transformations, it is obvious that the hydroxyl radicals in sulphuric acid must also be directly attached to sulphur.

The somewhat remarkable fact that many sulphates when heated retain one molecule of water of crystallisation (called "water of constitution") very persistently, whilst the other molecules are eliminated with relative ease, this phenomenon being observable with copper, manganese, ferrous, nickel, cobalt, magnesium and zinc sulphates, has led to a

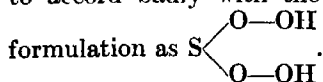
¹ Ramsay and Aston, *Trans. Chem. Soc.*, 1894, 65, 170; *Chem. News*, 1899, 79, 57.

suggestion that these monohydrates, of the general formula $M_2SO_4 \cdot H_2O$, are actually to be regarded as acid salts derived from a sulphuric acid of the constitution $O=S(OH)_2$, which corresponds with the composition of the monohydrate of sulphuric acid.¹

An alternative formula² for sulphuric acid, namely



has been suggested as representing more satisfactorily the hydrolytic activity of the substance, but the quadrivalent oxygen atom appears to accord badly with the stability of the acid, as also does such a



Detection and Estimation of Sulphuric Acid.—The usual dry test for a sulphate is reduction on charcoal in the presence of sodium or potassium carbonate; alkali sulphide in the fused product can easily be detected by moistening on a clean silver coin or by the application of other suitable tests.

An insoluble sulphate may be detected by the formation of *turpeth mineral* on the addition of a 10 per cent. solution of mercuric nitrate in dilute nitric acid (1 in 100); the small yellow tetragonal crystals of the basic sulphate may be identified microscopically. The reaction takes place immediately in the cold with calcium and mercurous sulphates, less readily with strontium and lead sulphates, whilst with barium sulphate boiling is necessary.³

For solutions containing sulphuric acid or a sulphate the reagent commonly applied is barium chloride, both when the test is to be qualitative and when quantitative. Precipitation is effected by the gradual addition of barium chloride to the boiling solution containing a little hydrochloric acid, but for the production of pure barium sulphate, and therefore in order to ensure accuracy, certain precautions must be observed.⁴ Nitrates, perchlorates, phosphates, trivalent metals and large quantities of salts of the alkali metals (particularly potassium) and of the alkaline earth metals are to be avoided, as they cause the precipitated barium sulphate to be rendered impure by occlusion of otherwise soluble substances.⁵ Such impurities may be accounted for partly by

¹ Geuther, *Annalen*, 1883, 218, 288; Colson, *Compt. rend.*, 1904, 139, 857.

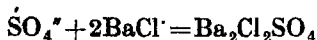
² Armstrong and Worley, *Proc. Roy. Soc.*, 1914, [A], 90, 73.

³ Demigès, *Bull. Soc. chim.*, 1918, [iv.], 23, 36.

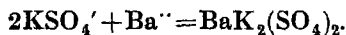
⁴ Consult the various text-books dealing especially with quantitative analysis.

⁵ Turner, *Phil. Trans.*, 1829, 119, 295; Rose, *Ann. Phys. Chem.*, 1861, [ii.], 113, 627; Mitscherlich, *J. prakt. Chem.*, 1861, 83, 456; Fresenius, *Zeitsch. anal. Chem.*, 1870, 9, 52; 1880, 19, 66; Marsh, *Chem. News*, 1889, 59, 309; Rapper, *Zeitsch. anorg. Chem.*, 1892, 2, 36; Richards and Parker, *ibid.*, 1895, 8, 413; Küster and Thiel, *ibid.*, 1900, 22, 424; Hulett and Duschak, *ibid.*, 1904, 30, 196; Pattinson, *J. Soc. Chem. Ind.*, 1905, 24, 7; van't Kruijs, *Chem. Weekblad*, 1909, 6, 735; Kato and Noda, *Mem. Coll. Sci. Eng. Kyoto*, 1909-10, 2, 217; von Fellenberg, *Chem. Zentr.*, 1915, ii., 1262; Winkler, *Zeitsch. angew. Chem.*, 1920, 33, 59, 159, 162, 287; Chatterjee, *Zeitsch. anorg. Chem.*, 1922, 121, 128; Moser and Kohn, *ibid.*, 1922, 122, 299; Hahn, *Ber.*, 1923, 56, [B], 1733; Kolthoff and van

reaction between the sulphion and the intermediate ions of any ternary electrolytes present ; ¹ thus, in the presence of excess of barium chloride the reaction



tends to increase the weight of the precipitate, whilst in the presence of potassium sulphate the opposite effect results from the reaction



Another source of error in this method of estimating sulphuric acid appears to be in the formation of the complex ion $[\text{Ba}_5(\text{SO}_4)_6]''$, the potassium salt of which has been isolated.² It is essential that the barium chloride be added slowly, and the precipitate should be collected from the hot solution and washed with hot aqueous acetic acid.³

Various modifications by which the reaction with barium chloride may be subjected to volumetric treatment have been suggested.⁴ Thus the precipitant may be added in excess and suitably back-titrated.⁵

Other reagents which may be applied to the volumetric determination of sulphuric acid and sulphates are barium chromate and benzidine. In the case of the former, the solution of sulphate is precipitated by a solution of barium chromate in hydrochloric acid ; on subsequent neutralisation of the filtrate, a quantity of chromic acid, equivalent to the barium sulphate which has been precipitated, remains in solution and may be estimated iodometrically.⁶ Benzidine, on the other hand, is an organic base which forms a very sparingly soluble sulphate ; the solution of mineral sulphate is treated with a solution of benzidine hydrochloride and the precipitated benzidine sulphate removed by filtration ; when subsequently suspended in pure water the benzidine sulphate undergoes hydrolysis to a sufficient extent to permit titration of the sulphuric acid with standard alkali.⁷ Lead nitrate may also be

Cittert, *Zeitsch. anal. Chem.*, 1923, 63, 392 ; Pavlov, *Ukraine Chem. J.*, 1926, 2, 353. For a micro-volumetric modification for very small quantities of sulphate, see Hamburger, *Biochem. Zeitsch.*, 1916, 77, 168.

¹ Kolthoff and Vogelenzang, *Pharm. Weekblad*, 1919, 56, 122.

² Balareff, *Zeitsch. anorg. Chem.*, 1922, 123, 69.

³ Karaoglanow, *Zeitsch. anal. Chem.*, 1918, 57, 77 ; Meillière, *J. Pharm. Chim.*, 1919, [vii.], 19, 296. See also Jensen, *Analyst*, 1928, 53, 136 ; Njegovan and Marjanović, *Zeitsch. anal. Chem.*, 1928, 73, 271 ; 74, 191.

⁴ Gay-Lussac, *Ann. Chim. Phys.*, 1828, 39, 337 ; Richards and Parker, *loc. cit.* ; Lang and Allen, *Trans. Chem. Soc.*, 1907, 91, 1370 ; Narugi and Bianchi, *Gazzetta*, 1906, 36, i., 347 ; Howden, *Chem. News*, 1918, 117, 383 ; Vansteenberger and Bauzil, *Ann. Chim. anal.*, 1918, 23, 210 ; Atkinson, *Analyst*, 1925, 50, 590, 1926, 51, 81 ; Roth, *Zeitsch. angew. Chem.*, 1926, 39, 1599 ; Schoch, *Ind. Eng. Chem.*, 1927, 19, 112.

⁵ See, for example, Kőszegi, *Zeitsch. anal. Chem.*, 1929, 77, 203 ; *Brit. Chem. Abs.*, 1929, A, 782.

⁶ Andrews, *Amer. Chem. J.*, 1889, 11, 567 ; *J. Amer. Chem. Soc.*, 1904, 32, 476 ; Quantin, *Compt. rend.*, 1886, 103, 402 ; *Bull. Soc. chim.*, 1889, [iii.], 1, 21 ; North, *Amer. J. Pharm.*, 1914, 86, 249 ; Pereira, *Anal. Fis. Quim.*, 1922, 20, 577. A similar process may be followed using lead nitrate and potassium chromate in place of barium chromate ; e.g., see Levöl, *J. prakt. Chem.*, 1853, 60, 384 ; Schwarz, *Zeitsch. anal. Chem.*, 1863, 2, 392 ; Oddo and Beretta, *Gazzetta*, 1909, 39, i., 671. See also Briwul, *Zeitsch. anorg. Chem.*, 1926, 156, 210.

⁷ Vaubel, *Zeitsch. anal. Chem.*, 1896, 35, 163 ; Müller, *Ber.*, 1902, 35, 1587 ; *Zeitsch. angew. Chem.*, 1903, 16, 653 ; Müller and Dürkes, *Zeitsch. anal. Chem.*, 1903, 42, 477 ; Raschig, *Zeitsch. angew. Chem.*, 1903, 16, 617, 818 ; Friedheim and Nydegger, *ibid.*, 1907, 20, 9 ; Haber, *Chem. Zeit.*, 1905, 29, 1227 ; Talenti, *Giorn. Chim. Ind. Appl.*, 1926, 8, 611 ; Vlastimil and Matula, *Chem. Zeit.*, 1926, 50, 486 ; Haase, *ibid.*, 1927, 51, 637 ; *Zeitsch. angew. Chem.*, 1927, 40, 595 ; Raschig, *ibid.*, 1927, 40, 864 ; Nydegger, *Chem. Zeit.*, 1928, 52, 318 ; Testoni, *Annali Chim. Appl.*, 1928, 18, 408.

used in the presence of alcohol to titrate sulphuric acid, a few drops of potassium iodide being added as indicator. Concordant but slightly low results are obtained.¹

Another volumetric process which has been recommended consists in reducing the sulphuric acid or sulphate (excepting barium sulphate) by heating with a mixture of hydriodic acid, phosphorus and phosphoric acid, absorbing the resulting hydrogen sulphide in a solution of zinc acetate, and estimating the precipitated zinc sulphide iodometrically.²

The importance of the determination of sulphuric acid and sulphates lies very largely in the fact that sulphur in various forms of combination, and also free sulphur, is frequently determined quantitatively by primary conversion into sulphuric acid or sulphate, followed by actual estimation in the latter form. For example, a convenient volumetric process applicable to the Carius method for determining sulphur in organic compounds is to neutralise the solution of sulphuric acid after removal of the excess of nitric acid by evaporation, and then add silver nitrate, by which the sulphate is converted into silver sulphate. This is separated from the excess of silver nitrate by means of its insolubility in alcohol, and is then estimated by dissolving in dilute nitric acid and titrating the silver with standard thiocyanate solution.³

For solutions containing sulphuric acid only, direct titration with standard alkali, and measurement of the specific gravity, are possible as methods of estimation, provided that the process in either case is, if necessary, preceded by suitable dilution (see p. 165). Thermometric methods have also been suggested, depending on the rise in temperature when the acid is mixed with water, or when titrated with barium chloride solution.⁴ The water content of the concentrated acid may be determined by similar titration with oleum which has been standardised thermometrically by 80 per cent. sulphuric acid (see p. 147).⁵

An electrometric method for determining soluble sulphates consists in precipitation of the latter by the addition of a measured excess of a standard solution of lead nitrate in the presence of alcohol, removing the lead sulphate by filtration, washing it with alcohol, and titrating the unchanged lead nitrate in the filtrate electrometrically with standard ferrocyanide solution.⁶

¹ Mindalev, *Zeitsch. anal. Chem.*, 1928, 75, 392.

² Auger and Gabillon, *Compt. rend.*, 1911, 152, 441.

³ Frerichs, *Arch. Pharm.*, 1903, 241, 159.

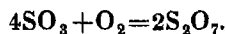
⁴ Droop Richmond and Merreywether, *Analyst*, 1917, 42, 273; Dean and Watts, *J. Amer. Chem. Soc.*, 1924, 46, 855.

⁵ Somiya, *Proc. Imp. Acad. Tokyo*, 1927, 3, 76; *J. Soc. Chem. Ind. Japan*, 1927, 30, 106.

⁶ Muller and Wertheim, *Zeitsch. anorg. Chem.*, 1924, 133, 411. For an electrometric method of determining small quantities of free sulphuric acid in the presence of sulphates, see Vulquin and Entat, *Ann. Chim. anal.*, 1917, 22, 61. For the determination of sulphate in the presence of other sulphur compounds, see Kurtenacker and Wollak, *Zeitsch. anal. Chem.*, 1927, 71, 37. For the determination of sulphate in animal and plant tissues and fluids, see Gortner and Hoffman, *Bot. Gaz.*, 1924, 77, 96; Lorber, *Biochem. Zeitsch.*, 1925, 163, 476; Denis and Leche, *J. Biol. Chem.*, 1925, 65, 561; in wool, see Hirst and King, *J. Text. Inst.*, 1926, 17, 101 T; Yamazaki, *Bull. Chem. Soc. Japan*, 1928, 3, 173; in water, see Zink and Hollandt, *Zeitsch. anal. Chem.*, 1927, 71, 386; Zaprometov, *Bull. Univ. Asie. Centr.*, 1927, p. 91, Kehren and Stommel, *Chem. Zeit.*, 1927, 51, 913, 934; Germuth, *J. Amer. Water Works Assoc.*, 1928, 19, 607; Fehn, Jander and Pfundt, *Zeitsch. angew. Chem.*, 1929, 42, 158.

Persulphuric Anhydride, Sulphur Heptoxide, S_2O_7 , (?)

In 1878, Berthelot, by submitting a mixture of sulphur dioxide or trioxide with excess of oxygen under compression to a silent electric discharge of high potential, obtained a product which he regarded as sulphur heptoxide:¹



At the ordinary temperature this was in the form of a viscous liquid which could be frozen to a crystalline solid of m.pt. 0° C. Although the heptoxide is an exothermic substance with respect to its elements,² it is endothermic as regards sulphur trioxide and oxygen.³ As might be expected, therefore, it is very unstable, and after a few days gradually decomposes into sulphur trioxide and oxygen, the process being accelerated by rise in temperature and also by contact with platinum black.

According to Berthelot the substance fumed in moist air, owing to formation of sulphur trioxide, and reacted vigorously with water with partial decomposition, oxygen being liberated. A portion, however, dissolved in the manner of an ordinary acid anhydride, with the production of perdisulphuric acid, which can undergo further successive decomposition into permonosulphuric acid and hydrogen peroxide.⁴ Baryta water similarly gives rise to barium sulphate and barium perdisulphate, the latter being soluble in water.

Sulphur dioxide is oxidised by the heptoxide with formation of sulphuric anhydride:



Berthelot's experiments and conclusions have not been fully confirmed, however. According to Meyer and his co-workers,⁵ the crystalline product described is only formed when sulphur trioxide is present in excess, and may be regarded as an equimolecular mixture of sulphur trioxide and *sulphur tetroxide*, SO_4 . There is evidence that the latter compound is produced during the oxidation of cold solutions of sulphuric acid (2.35 molar) or of alkali sulphates.⁶

Maisin,⁷ on repeating Berthelot's experiment with a mixture of sulphur dioxide and oxygen, observed that the pressure in the discharge tube rapidly fell and an opaque solid formed on the walls of the vessel. Sometimes an oil was obtained. The product was relatively stable, did not fume in moist air, and dissolved in water without any vigorous action, forming a strongly oxidising solution. Unlike Berthelot's product, it was insoluble in sulphuric acid. The residual gases in the tube gave the reactions of the sulphate ion. Maisin concluded that the product was not the heptoxide, nor did its behaviour conform with Meyer's opinion that it was a mixture of the trioxide and tetroxide; he suggested, however, that it appeared to be a definite compound of composition S_3O_{11} , which might be regarded as a mixed anhydride of permono- and perdisulphuric acids.

¹ Berthelot, *Compt. rend.*, 1878, 86, 20, 71, 277; *Ber.*, 1879, 12, 275.

² Berthelot, *Compt. rend.*, 1880, 90, 331.

³ Giran, *ibid.*, 1905, 140, 1704.

⁴ Berthelot, *ibid.*, 1891, 112, 1418; Richarz, *Ber.*, 1888, 21, 1669.

⁵ Meyer, Bailleul and Henkel, *Ber.*, 1922, 55, [B], 2923.

⁶ Fichter and Humpert, *Helv. Chim. Acta*, 1926, 9, 602; Fichter and Bladergroen, *ibid.*, 1927, 10, 553.

⁷ Maisin, *Bull. Soc. chim. Belg.*, 1928, 37, 326.

Persulphuric Acid or Perdisulphuric Acid, $\text{H}_2\text{S}_2\text{O}_8$.

When cold aqueous sulphuric acid of suitable concentration is electrolysed in a divided cell, a solution of perdisulphuric acid is obtained at the anode.¹ The most favourable concentration of sulphuric acid is 45 to 60 per cent., but even with this the yield is far from quantitative, and, indeed, after a time further electrolysis actually effects a decrease in the quantity of perdisulphuric acid. If the sulphuric acid is too weak the anodic product may be only oxygen, whilst with too concentrated an acid the perdisulphuric acid will undergo conversion into permonosulphuric acid, which decomposes readily. The addition to the electrolyte of a few drops of hydrochloric acid,² or of a solution of perchloric acid, or of an alkali perchlorate,³ has been found to favour the formation of the perdisulphuric acid; it is also advisable that the platinum anode should be smooth or polished and not rough or platinised.

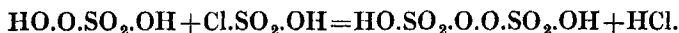
By treating the crude solution of perdisulphuric acid with the requisite quantity of barium carbonate or hydroxide, the unaltered sulphuric acid can be removed and a pure aqueous solution of perdisulphuric acid obtained.⁴

The formation of the perdisulphuric acid in the electrolysis of sulphuric acid is due to the coupling together of the discharged HSO_4' ions at the anode; it is for this reason that very dilute sulphuric acid, which is mainly dissociated into H^+ and SO_4^{2-} ions, is unsuited for the electrolytic preparation. A 70 per cent. yield is obtained by large scale production from acid of strength 500 grams per litre.⁵

Perdisulphuric acid may also be isolated by allowing well-cooled chlorosulphonic acid to react with a semi-molecular proportion of anhydrous hydrogen peroxide :⁶



This result is important as providing clear demonstration of the peroxidic structure of perdisulphuric acid. Caro's acid may be used in place of hydrogen peroxide :



The hydrogen chloride is removed by keeping in a desiccator under reduced pressure, when the required acid remains as a mass of white crystals.

The Perdisulphates.—A similar process to the electrolytic preparation of perdisulphuric acid is possible for the preparation of the perdisulphates. The corresponding alkali hydrogen sulphate or a mixture of the normal sulphate and sulphuric acid in cold aqueous solution is electrolysed in a cell so arranged that the anode and cathode are

¹ Berthelot, *Compt. rend.*, 1878, 86, 20, 71; *Ber.*, 1879, 12, 275.

² Petrenko, *J. Russ. Phys. Chem. Soc.*, 1904, 36, 1081; Richarz, *Ann. Phys. Chem.*, 1885, [iii.], 24, 183. See also Moldenhauer, *Zeitsch. Elektrochem.*, 1906, 11, 307; Müller and Schellhaas, *ibid.*, 1907, 13, 257; Müller and Emslander, *ibid.*, 1912, 18, 752.

³ Mazzucchelli, *Gazzetta*, 1924, 54, 1010; Mazzucchelli and Romani, *ibid.*, 1927, 57, 574.

⁴ Berthelot, *Compt. rend.*, 1891, 112, 1418; Elbs and Schönherr, *Zeitsch. Elektrochem. and Elektrochem.*, 1895, 2, 245, 417, 468; Richarz, *Ber.*, 1888, 21, 1669; Marshall, *J. Soc. Chem. Ind.*, 1897, 16, 396; Stark, *Zeitsch. physikal. Chem.*, 1899, 29, 385.

⁵ *British Patent*, 265141 (1926).

⁶ d'Ans and Friederich, *Ber.*, 1910, 43, 1880.

separated by a porous diaphragm,¹ or at least arranged so that the cathode gases shall not pass near the anode;² a convenient experimental apparatus is represented in the diagram (fig. 13). The yield of alkali perdisulphate is increased by the presence of nickel sulphate, aluminium sulphate,³ alkali fluoride,⁴ potassium thiocyanate or

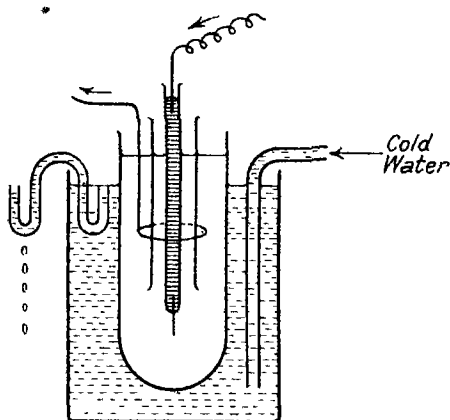
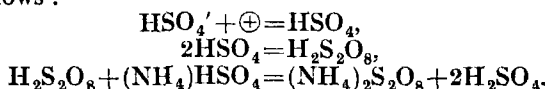


FIG. 13.—Apparatus for Preparation of Perdisulphates

potassium ferrieyanide⁵ in the electrolyte, and also by the application of a high current density at the anode, which should therefore be as small as is convenient. A platinum anode is commonly used, and this should be of smooth metal;⁶ electrodes of aluminium and tin have also been recommended.⁷

As in the electrolytic formation of perdisulphuric acid, the first anodic product is the discharged HSO_4' ion, which by coupling then gives rise to perdisulphuric acid. If the metal perdisulphate is less soluble than the acid sulphate, it crystallises from the solution; this is

the case in the electrolysis of a concentrated solution of potassium or ammonium hydrogen sulphate,⁸ the changes in the case of the latter salt being as follows:



Ammonium perdisulphate has also been prepared⁹ by passing fluorine into a cold saturated aqueous solution of ammonium hydrogen sulphate; ozonised oxygen escapes as oxidation proceeds and crystals of the per-sulphate slowly separate.

The perdisulphates of the alkaline earth metals may be prepared by grinding together, with a little water, molecular proportions of the metal oxide and ammonium perdisulphate,¹⁰ and drying the mixture in a vacuum. The resulting mass is carefully powdered and the metal

¹ Marshall, *Trans. Chem. Soc.*, 1891, 59, 771; *J. Soc. Chem. Ind.*, 1897, 16, 346; Berthelot, *Compt. rend.*, 1892, 114, 875; Forster and Smith, *J. Amer. Chem. Soc.*, 1899, 21, 934; Haber and Klemenov, *Zeitsch. Elektrochem.*, 1914, 20, 485.

² Müller and Friedberger, *Zeitsch. Elektrochem.*, 1902, 8, 230.

³ Marshall, *loc. cit.*

⁴ Konsortium f. Elektrochem. Ind., *German Patent*, 155805 (1905).

⁵ Vereinigte Chem. Werke Aktiengesellschaft, *German Patents*, 205067, 205068, 205069 (1907); Schall and Andrich, *Chem. Zeit.*, 1912, 36, 645; Blumer, *Zeitsch. Elektrochem.*, 1911, 17, 965.

⁶ Marshall, *loc. cit.*; Levi, *Zeitsch. Elektrochem.*, 1903, 9, 427.

⁷ Bayer & Co., *German Patent*, 271642 (1914).

⁸ For optimum conditions for the electrolytic preparation of ammonium perdisulphate, see Salauze, *Bull. Soc. chim.*, 1923, 33, [iv.], 1738. See also Essin and Krylow, *Zeitsch. Elektrochem.*, 1927, 33, 107; 1928, 34, 758.

⁹ Fichter and Humpert, *Helv. Chim. Acta*, 1926, 9, 467, 521, 602. The action of fluorine on K_2SO_4 and KHSO_4 is also described.

¹⁰ Erdenbrecher, *Chem. Zeit.*, 1924, 48, 189.

perdisulphate extracted by solution in absolute alcohol, from which it may be obtained by the addition of absolute ether, or by evaporation in a vacuum.

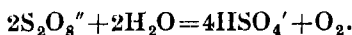
Physical Properties of Perdisulphuric Acid.—Pure perdisulphuric acid, prepared as described, is a hygroscopic crystalline solid which melts near 65° C. with partial decomposition. It gradually decomposes at the ordinary temperature with liberation of oxygen.

When dissolved directly in water the reaction is sufficiently vigorous to cause partial conversion into permonosulphuric acid; if, however, an ether solution of the acid is placed on cold water, the process of dissolution in the water occurs more gently and an aqueous solution of perdisulphuric acid is obtainable from which the potassium salt can be obtained by careful neutralisation.

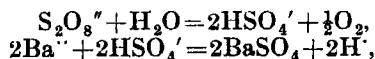
Like the so-called "sulphur heptoxide," the acid is exothermic with respect to its elements but endothermic as regards its decomposition products, sulphuric acid and oxygen.

Chemical Properties.—The chemical properties of perdisulphuric acid are inferred mainly from the behaviour of its salts; these may be derived not only from the various metals but also from organic bases, quinine, for instance, yielding an acid perdisulphate, $C_{20}H_{24}O_2N_2 \cdot H_2S_2O_8$, and a normal perdisulphate $(C_{20}H_{24}O_2N_2)_2 \cdot H_2S_2O_8$, both crystalline solids.¹ Strychnine perdisulphate is so sparingly soluble in water that ammonium perdisulphate has been suggested as an antidote for strychnine poisoning.

The metal perdisulphates are all fairly soluble in water, those of the alkali metals, including ammonium, being more stable than the free acid or other salts. All the salts, however, tend to decompose very slowly when dry and protected from sunlight, and more rapidly in solution, especially on warming, giving rise to the corresponding sulphates together with sulphuric acid and oxygen.² The decomposition of the salts in aqueous solution is a unimolecular reaction;³ platinum black slightly accelerates the decomposition, as also do alkalis, nitrates and phosphates, whilst acids have a marked effect, although no autocatalysis occurs during the decomposition of a perdisulphate if the metal forms a soluble hydrogen sulphate, since the HSO_4' ion exerts no marked effect:



With aqueous barium perdisulphate the decomposition is at first catalysed by the formation of free sulphuric acid:



but when the reaction has gone half-way, all the barium has been precipitated and the reaction becomes approximately unimolecular.⁴

The decomposition of the alkali perdisulphates in aqueous solution is retarded by the presence of added alkali sulphates. The influence

¹ Wolfenstein and Wolff, *Ber.*, 1904, 37, 3213; 1908, 41, 717; also Fosse and Bertrand, *Compt. rend.*, 1904, 139, 600; Vitali, *Boll. Chim. Farm.*, 1903, 42, 273, 321.

² Baeyer and Villiger, *Ber.*, 1901, 34, 856; Vitali, *Boll. Chim. Farm.*, 1903, 42, 273; Elbs and Neber, *Chem. Zeit.*, 1921, 45, 1113.

³ Tarugi, *Gazzetta*, 1902, 32, ii., 383. Levi and Mighorini, *ibid.*, 1906, 36, ii., 599.

⁴ Green and Masson, *Trans. Chem. Soc.*, 1910, 97, 2083.

of neutral sulphate is greater than that of hydrogen sulphate,¹ and the sodium ion appears to retard the decomposition of the perdisulphate ion to a smaller extent than the potassium ion. This observation is in accordance with the fact that increasing concentration of added sodium hydroxide accelerates the decomposition of sodium perdisulphate to a greater extent than similar addition of potassium hydroxide.²

On account of the effect of acids on the rate of decomposition, aqueous perdisulphuric acid itself decomposes much more rapidly than aqueous solutions of its alkali salts; in the presence of cold sulphuric acid of about 40 per cent. concentration, perdisulphuric acid and its salts give rise to permonosulphuric acid, which subsequently decomposes into sulphuric acid and oxygen or hydrogen peroxide.³ This fact is made use of in the technical production of hydrogen peroxide, the process consisting in distilling either the solution of perdisulphuric acid obtained by electrolysis of sulphuric acid, or a mixture of potassium perdisulphate and dilute sulphuric acid.

Aqueous hydrogen peroxide also causes the liberation of oxygen from perdisulphate solutions, probably on account of interaction with Caro's acid first formed.⁴ The reaction is considerably retarded by the presence of acid.

The perdisulphates of the alkali metals and ammonium crystallise in the anhydrous condition and when heated alone undergo decomposition with formation of sulphate, sulphur trioxide and oxygen:



The ammonium salt is less stable than the potassium salt. Rapid decomposition does not take place even in the presence of 10 per cent. of organic matter.⁵ Barium and lead perdisulphates contain water of crystallisation and therefore on decomposition yield sulphuric acid in place of sulphur trioxide. The perdisulphates of the heavier metals also form additive compounds with ammonia, for example $ZnS_2O_8 \cdot 4NH_3$ and $CdS_2O_8 \cdot 6NH_3$, and even with organic bases.⁶

Oxidising Properties.—Both acid and salts are characterised by great oxidising power. Manganese, lead, nickel and cobalt salts in aqueous solution in the presence of alkali are oxidised to dioxides.⁷ Metallic silver and silver nitrate react with sodium or potassium perdisulphate to form a peroxide containing more oxygen than Ag_2O_2 ; ⁸ some sulphate is formed and at the same time the acidity of the solution increases. Ammonium perdisulphate does not give silver peroxide but is itself oxidised to nitric acid. Possibly on account of the instability of silver perdisulphate, the presence of a silver salt greatly increases the oxidising activity of the alkali perdisulphates.

¹ Kailan and Olbrich, *Monatsh.*, 1927, 47, 449; Kailan and Leisek, *ibid.*, 1928, 50, 403. Cf. Green and Masson, *loc. cit.*

² Kailan and Leisek, *loc. cit.* Cf. Levi and Migliorini, *loc. cit.*

³ Baeyer and Villiger, *Ber.*, 1901, 34, 856; Palme, *Zeitsch. anorg. Chem.*, 1920, 112, 97.

⁴ Palme, *loc. cit.*; Friend, *Trans. Chem. Soc.*, 1906, 89, 1092; Kastle and Loevenhart, *Amer. Chem. J.*, 1903, 29, 563; Price, *Ber.*, 1902, 35, 291.

⁵ Agde and Alberti, *Chem. Zeit.*, 1928, 52, 229.

⁶ Barbieri and Calzolari, *Zeitsch. anorg. Chem.*, 1911, 71, 347.

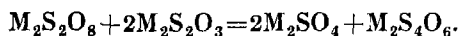
⁷ Marshall, *Chem. News*, 1901, 83, 76.

⁸ Higson, *Trans. Chem. Soc.*, 1921, 119, 2048. See also Austin, *ibid.*, 1911, 99, 262; Levi, Migliorini and Ercolini, *Gazzetta*, 1908, 38, i, 583; Tarugi, *ibid.*, 1902, 32, ii, 383; Marshall, *Proc. Roy. Soc. Edin.*, 1900, 23, 168; *J. Soc. Chem. Ind.*, 1897, 16, 396; also King, *J. Amer. Chem. Soc.*, 1927, 49, 2689.

Chlorides, bromides and iodides in solution are gradually oxidised with formation of the halogen element, the oxidation in the case of iodides extending even to the production of iodate. In the presence of dilute nitric acid even silver chloride, bromide and iodide undergo partial oxidation to the corresponding halogenates, whilst a small quantity of a silver salt so aids the oxidising process that soluble chlorides and bromides also are to some extent converted into the halogenates.¹ The oxidation of iodides to free iodine is accelerated in a marked manner by quite minute quantities of ferrous or copper salts,² and also by the presence of gelatin.³ Iodates are further partially converted into periodates.⁴

In aqueous solution, manganous salts are oxidised to manganese dioxide,⁵ and if silver nitrate is present as catalyst, to permanganate; ⁶ the latter change constitutes *Marshall's reaction*. Chromium solutions in a similar manner give rise to chromate,⁷ even without a catalyst. Ferrous and cerous salts are converted into ferric and ceric salts, respectively, and phosphites are oxidised to phosphates.

Thiosulphates are converted into tetrathionates, or if excess of thiosulphate is used, into trithionates (see p. 214):



Consequently, the use of potassium perdisulphate has been suggested to effect the removal of sodium thiosulphate from photographic negatives after "fixing."⁸

Almost all the metals, with the exception of gold and platinum, are attacked by aqueous perdisulphate solutions, the metal giving rise to undissolved oxide or dissolving.⁹ Iron, zinc, copper, cadmium, nickel, cobalt and magnesium all pass into solution, the last-named vigorously. In no case is any considerable quantity of hydrogen evolved. The presence of ammonia is advantageous in certain cases, especially that of copper. By dissolving the respective metals in cold aqueous solutions of alkali perdisulphates the following double salts have been obtained: ¹⁰ $M(RO)_2(SO_2O)_2 \cdot 6H_2O$, where $R=K$ or NH_4 , and $M=Mg, Zn, Cd, Fe^{++}, Ni$ or Co ; also $M(NaO)_2(SO_2O)_2 \cdot 4H_2O$, where $M=Mg, Zn, Cd$ or Fe^{++} . In the case of manganese, chromium, molybdenum, selenium and arsenic, solution occurs with formation of the corresponding acidic radicals.¹¹

Not only is platinum unattacked by perdisulphates, but it only

¹ Dittrich and Bollenbach, *Ber.*, 1905, 38, 747.

² Federlin, *Zeitsch. physikal. Chem.*, 1902, 41, 565; Price, *ibid.*, 1898, 27, 474.

³ Rawling and Glassett, *J. Physical Chem.*, 1925, 29, 414. The kinetics of the reaction between persulphate and iodide have been studied by von Kiss and von Zombory, *Rec. Trav. chim.*, 1927, 46, 225; 1929, 48, 508.

⁴ Müller and Jacob, *Zeitsch. anorg. Chem.*, 1913, 82, 308.

⁵ Marshall, *Chem. News*, 1901, 83, 76; Dittrich and Hassel, *Ber.*, 1903, 36, 284, 1423.

⁶ Marshall, *loc. cit.*; Stehmann, *J. Amer. Chem. Soc.*, 1902, 24, 1204.

⁷ Dakin, *J. Soc. Chem. Ind.*, 1902, 21, 848; Yost, *J. Amer. Chem. Soc.*, 1926, 48, 152.

⁸ See, however, Marshall, *Trans. Edin. Phot. Soc.*, 1902, 2, 117; Clark, *Brit. J. Phot.*, 1927, 74, 121. See also Higson, *Phot. J.*, 1921, 61, 237.

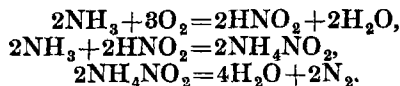
⁹ Marshall, *J. Soc. Chem. Ind.*, 1897, 16, 396.

¹⁰ Aschan and Petrelius, *Finska Kemistisamf. Medd.*, 1928, 37, 40; *Chem. Zentr.*, 1928, ii., 1866.

¹¹ Levi, Migliorini and Ercolini, *Gazzetta*, 1908, 38, i., 583; Tarugi, *ibid.*, 1903, 33, i., 127; Turrentine, *J. Physical Chem.*, 1907, 11, 623.

slightly influences the rate of decomposition of these salts or of free perdisulphuric acid.¹

Ammonia in aqueous solution is vigorously oxidised to nitrogen by perdisulphates in the presence of silver nitrate² or copper sulphate.³ In the latter case the ammonia is first oxidised to nitrous acid, and the decomposition proceeds, as heat develops, according to the scheme :



In an aqueous solution containing ammonium perdisulphate only, the ammonium radical is gradually converted into nitric acid, this reaction explaining why the decomposition of ammonium perdisulphate diverges somewhat from the simple unimolecular course⁴ (p. 183). Hydrazine in aqueous solution, prepared by the addition of an alkali to hydrazine sulphate, is similarly oxidised to nitrogen by perdisulphates :⁵



Many organic substances are oxidised by the perdisulphates. Potassium cyanide in the presence of ammonia is converted into urea,⁶ due to the primary formation of potassium cyanate, which then undergoes change into urea by way of ammonium cyanate. Potassium ferrocyanide when heated with a perdisulphate yields a mixture of hydrogen cyanide and cyanogen.⁷ Ethyl alcohol when warmed with a perdisulphate rapidly forms acetaldehyde.⁸ Certain benzene derivatives undergo oxidation, sometimes with formation of coloured products,⁹ colour reactions being exhibited by *p*-aminophenol, *p*-phenylenediamine, α - and β -naphthols, and diaminophenol; occasionally, as with quinol, the oxidation process is found to be accompanied by the introduction of sulphur into the molecule. In acid solution, aniline is oxidised to aniline black.¹⁰ On the other hand, many of the natural organic colouring substances are bleached by the perdisulphates. Oxalic acid, as might be expected, gives carbon dioxide; the reaction is very sensitive to the presence of silver ions, being accelerated to a greater degree than would be expected from the influence of silver on the reaction with other reducing agents.¹¹

Molecular Weight and Constitution.—The electrical conductivity of aqueous solutions of potassium perdisulphate supplies distinct evidence of the dibasicity of the corresponding acid.¹² This is confirmed by molecular weight determinations made by the cryoscopic method

¹ See also Price, *Ber.*, 1902, 35, 291.

² Marshall, *Proc. Roy. Soc. Edin.*, 1900, 23, 163; Kempf, *Ber.*, 1905, 38, 3972; King, *J. Amer. Chem. Soc.*, 1927, 49, 2689.

³ Scagliarini and Torelli, *Gazzetta*, 1921, 51, ii., 277.

⁴ Marshall and Inglis, *Proc. Roy. Soc. Edin.*, 1902, 24, 88.

⁵ Pannain, *Gazzetta*, 1904, 34, i., 500.

⁶ Tarugi, *Gazzetta*, 1902, 32, ii., 383.

⁷ Bellucci and Ricca, *Atti I. Congr. naz. Chim. pur. appl.*, 1923, p. 400.

⁸ Willstätter, *Ber.*, 1903, 36, 1828.

⁹ Namias, *L'Orosi*, 1900, 23, 218.

¹⁰ Caro, *Zeitsch. angew. Chem.*, 1898, 11, 845. For other organic oxidation effects, see Austin, *Trans. Chem. Soc.*, 1911, 99, 282; Marshall, *Proc. Roy. Soc. Edin.*, 1900, 23, 168; Marshall and Inglis, *ibid.*, 1902, 24, 88; Elbs, *Zeitsch. angew. Chem.*, 1897, 10, 195.

¹¹ King, *loc. cit.*

¹² Marshall, *Trans. Chem. Soc.*, 1891, 59, 771; *J. Soc. Chem. Ind.*, 1897, 16, 396; Bredig, *Zeitsch. physikal. Chem.*, 1893, 12, 230; Moeller, *ibid.*, 1893, 12, 555; Loewenherz, *ibid.*, 1895, 18, 70; *Chem. Zeit.*, 1892, 16, 838.

with solutions of the salt in water ¹ and also in fused sodium sulphate decahydrate ² ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), which give results agreeing with a molecule $\text{K}_2\text{S}_2\text{O}_8$. Direct evidence in favour of this formula is also forthcoming from the synthesis of perdisulphuric acid by the sulphonation of hydrogen peroxide (p. 181). This synthetic reaction also pro-

vides convincing evidence of the constitution $\text{HO}-\overset{\overset{\text{O}}{\parallel}}{\text{S}}-\text{O}-\text{O}-\overset{\overset{\text{O}}{\parallel}}{\text{S}}-\text{OH}$,

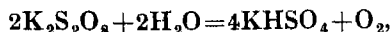
the probability of which had been realised much earlier ³ and which represents perdisulphuric acid as derived from hydrogen peroxide by the substitution of a sulphonic acid group, $-\text{SO}_2\text{OH}$, for each hydrogen atom.

Detection and Estimation.—The oxidising properties of perdisulphuric acid and its salts render detection easy; distinction from hydrogen peroxide can be made by means of chromic or permanganic acid or a sulphuric acid solution of titanium dioxide, towards all of which perdisulphuric acid is inactive. Strychnine nitrate is a convenient reagent for the perdisulphates, giving a precipitate of strychnine perdisulphate, $(\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2)_2 \cdot \text{H}_2\text{S}_2\text{O}_8 \cdot \text{H}_2\text{O}$, which at 17°C . dissolves in water to the extent of only 0.04 gram (calculated as anhydrous salt) per 100 c.c., although it dissolves more readily in acids. ⁴ Various colour reactions are also available for the detection of perdisulphates; guaiacum tincture gives a blue coloration; ⁴ aniline sulphate with a neutral solution gives a crystalline orange-brown precipitate which dissolves in hydrochloric acid to a yellow solution, the colour changing to violet on heating; ⁵ a 2 per cent. solution of benzidine in alcohol gives a perceptible blue colour even with solutions containing only one part of perdisulphate per million, a yellow coloration or yellow precipitate being obtained with stronger solutions.

The most generally trustworthy procedure for the estimation of a perdisulphate is to boil the neutralised solution for half an hour and then measure the resulting acidity; ⁶ the method may be modified by the successive addition of a neutralised solution of hydrazine sulphate and of a known volume of standard alkali hydroxide, when the sulphuric acid first produced during the course of the reaction



can be determined by titrating the excess alkali. ⁷ In the latter method methyl orange must be used throughout as indicator, and it will be noticed that the resulting acidity is greater than in the case of the simple decomposition of the perdisulphate,



¹ Moeller, *loc. cit.*; Loewenherz, *loc. cit.*; Berthelot, *Compt. rend.*, 1892, 114, 876.

² Loewenherz, *loc. cit.*

³ Traube, *Ber.*, 1892, 25, 95; Melikov and Pissarjewski, *Zeitsch. anorg. Chem.*, 1898, 18, 59.

⁴ Vitali, *Boll. Chim. Farm.*, 1903, 42, 273, 321.

⁵ Caro, *Zeitsch. angew. Chem.*, 1898, 11, 845.

⁶ Vitali, *loc. cit.*; Tarugi, *Gazzetta*, 1902, 32, ii., 383; Mario and Brunel, *Bull. Soc. chim.*, 1903, [iii.], 30, 930.

⁷ Rimini, *Atti R. Accad. Lincei*, 1906, [v.], 15, ii., 320.

on account of the acid previously combined with the hydrazine. As has already been mentioned, the decomposition of ammonium perdisulphate is not wholly of the type represented in the last equation, the ammonium radical undergoing partial oxidation, and if it is desired to examine ammonium perdisulphate by the first method, a measured excess of standard alkali must be added at the commencement in order to convert the ammonium salt into the more stable salt of an alkali metal.¹

Oxidation processes involving the subsequent titration of an excess of ferrous sulphate,² oxalic acid (in the presence of silver sulphate as catalyst),³ titanous chloride,⁴ or of the quantity of iodine liberated from potassium iodide,⁵ are also available but are less satisfactory. In the last-named method a large excess of potassium iodide is necessary to obtain complete reaction in a short time. The reaction may be accelerated by the addition of potassium chloride⁶ or ammonium chloride; with 20 per cent. by weight of the latter salt present a large excess of the iodide is not necessary and the liberated iodine may be titrated after fifteen minutes.⁷

It may be remarked that although perdisulphates alone in acid solution do not affect potassium permanganate, they interfere with the titration of hydrogen peroxide by this reagent, a portion of the peroxide being destroyed by the perdisulphate.⁸ To estimate the total active oxygen in mixtures of perdisulphate and hydrogen peroxide, gasometric methods are most suitable, or the iodometric method may be used, the mixture being kept below 20° C. and out of the direct rays of the sun, and the liberated iodine being titrated after twenty-four hours.⁹

The main application of the perdisulphates is in analytical chemistry; other directions in which they find use are mentioned under the description of their properties. Because of their oxidising and bleaching action they are used in the textile and dyeing industries, and for bleaching soap. They are also used for deodorising whale and fish oils and animal fats in order to render them suitable for soap making.

Permonosulphuric Acid or Caro's Acid, H_2SO_5 .

Preparation.—(1) *From Perdisulphates.*—In 1878 Berthelot noticed that the solution obtained by adding sulphur heptoxide (p. 180) to water oxidised potassium iodide almost instantaneously, and in 1889 Traube¹⁰ observed that an electrolysed (anodic) solution of sulphuric acid possessed the same property, which he attributed to the presence of a super-oxide SO_4 (cf. p. 180). The reaction with potassium iodide cannot have been due to perdisulphuric acid, because this liberates iodine quite slowly. In 1898 Caro obtained a similar oxidising solution

¹ Tarugi, *loc. cit.*

² Le Blanc and Eckhardt, *Zeitsch. Elektrochem.*, 1898, 5, 355.

³ Kempf, *Ber.*, 1905, 38, 3965.

⁴ Knecht and Hibbert, *ibid.*, p. 3324.

⁵ Mondolfo, *Chem. Zeit.*, 1899, 23, 699; Namias, *L'Orosi*, 1900, 23, 218; Peters and Moody, *Amer. J. Sci.*, 1901, [iv.], 12, 367.

⁶ von Zombory, *Zeitsch. anal. Chem.*, 1928, 73, 217.

⁷ Schwicker, *ibid.*, 1928, 74, 433.

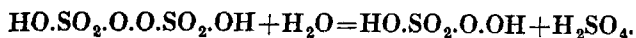
⁸ Friend, *Trans. Chem. Soc.*, 1906, 89, 1092. See also Pannain, *Gazzetta*, 1904, 34, i., 500; Scagliarini and Torelli, *ibid.*, 1921, 51, ii., 277, for suggested gasometric methods.

⁹ Lubarski and Dikova, *J. Russ. Phys. Chem. Soc.*, 1928, 60, 735.

¹⁰ Traube, *Ber.*, 1889, 22, 1518; 1891, 24, 1764; 1892, 25, 95.

by the action of cold concentrated sulphuric acid on ammonium perdisulphate.¹

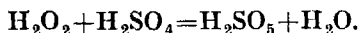
In all the foregoing cases the first product is perdisulphuric acid, but this tends to undergo unimolecular change, which is greatly accelerated by the presence of excess of sulphuric acid, with formation of permonosulphuric acid,² frequently called Caro's acid :



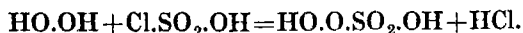
Whether the solution obtained by the electrolysis of sulphuric acid will straightway contain permonosulphuric acid or will only develop it on keeping is dependent on the concentration of the acid present.

The usual method of preparation consists in intimately mixing potassium or ammonium perdisulphate with approximately twice its weight of concentrated sulphuric acid at about -10°C. ; after keeping for one hour, the mixture is diluted by pouring on to powdered ice and excess of sulphuric acid removed by addition of the requisite quantity of barium hydrogen phosphate, the carbonate and hydroxide of this metal being unsuitable on account of their decomposing effect on the acid.³ After concentration *in vacuo*, solutions containing active oxygen equivalent to about 18 grams of H_2SO_5 per litre are obtained.⁴ It is possible, however, to obtain solutions of the potassium salt approaching gram-molecular strength by a modification of this method.⁵ The potassium perdisulphate is triturated with a considerably smaller quantity of the concentrated acid (13 c.c. for 20 grams salt), and the neutralisation of the ice-containing diluted solution is effected by adding first potassium carbonate solution and finally a little anhydrous potassium carbonate. It is essential that local rises in temperature during neutralisation should be avoided, since these undoubtedly cause decomposition of Caro's acid. The solutions obtained are free from hydrogen peroxide.

(2) *From Hydrogen Peroxide.*—The formation of a strongly oxidising acid was also observed by Berthelot in 1878⁶ when he allowed sulphuric acid to react with hydrogen peroxide. The reaction, which was re-investigated by Baeyer and Villiger⁷ in 1900, is apparently unimolecular if a large excess of concentrated sulphuric acid is used,⁸ this behaviour according well with the equation



Pure permonosulphuric acid may be obtained by the gradual addition of the theoretical quantity of anhydrous hydrogen peroxide to cold pure chlorosulphonic acid :⁹



¹ Caro, *Zeitsch. angew. Chem.*, 1898, **11**, 845.

² Baeyer and Villiger, *Ber.*, 1901, **34**, 853; 1900, **33**, 124, 858, 1569. See also Mugdan, *Zeitsch. Elektrochem.*, 1903, **9**, 719, 980; Tarugi, *Gazzetta*, 1903, **33**, i., 127.

³ Baeyer and Villiger, *Ber.*, 1899, **32**, 3625; 1900, **33**, 2488; 1901, **34**, 853; Bamberger, *ibid.*, 1900, **33**, 1781.

⁴ Price, *Trans. Chem. Soc.*, 1906, **89**, 53.

⁵ Vallance, *J. Soc. Chem. Ind.*, 1926, **45**, 66 T.

⁶ Berthelot, *Ann. Chim. Phys.*, 1878, [v.], **14**, 360.

⁷ Berthelot, *loc. cit.*; also Lowry and West, *Trans. Chem. Soc.*, 1900, **77**, 950.

⁸ Ahrie, *J. prakt. Chem.*, 1909, **79**, 129; *Zeitsch. angew. Chem.*, 1909, **22**, 1713.

⁹ d'Ans and Friederich, *Ber.*, 1910, **43**, 1880.

When evolution of hydrogen chloride has ceased, any gas remaining in solution is drawn off at the pump; the residue of Caro's acid then solidifies.

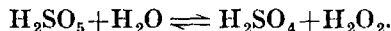
Properties.—Pure permonosulphuric acid is an unstable crystalline solid which slowly decomposes even at low temperatures; it melts with slight decomposition at 45° C.

For ordinary purposes aqueous solutions of the acid are sufficient; these possess an odour resembling that of hypochlorous acid.

Although permonosulphuric acid is formed from acid-containing solutions of perdisulphuric acid, the latter is the more stable in neutral and alkaline solutions.

No salt of permonosulphuric acid has been obtained in a pure condition. The acid is monobasic, only one hydrogen atom being dissociable, the ions being H^+ and $\text{SO}_5\text{H}'$.¹

In solution, permonosulphuric acid tends to undergo hydrolysis to sulphuric acid and hydrogen peroxide: ²



As might be expected of such a reaction, the change is accelerated by the presence of finely divided or colloidal platinum, which facilitates the decomposition of the hydrogen peroxide and so removes it from the sphere of the reaction. The addition of hydrogen peroxide aids the decomposition of permonosulphuric acid in the presence of colloidal platinum, equivalent quantities of oxygen coming from the hydrogen peroxide and the acid.³ Like the conversion of perdisulphuric acid into permonosulphuric acid, the hydrolysis of the latter acid, as represented in the foregoing equation, occurs more rapidly in the presence of concentrated sulphuric acid, whilst in sulphuric acid of 8 per cent. concentration permonosulphuric acid is relatively stable; in the preparation of this acid from a perdisulphate, therefore, it is advisable to dilute the reaction product so that the sulphuric acid approximately attains this concentration. Permonosulphuric acid is also fairly stable in aqueous phosphoric acid solution ² (see p. 189).

The usual method of estimating hydrogen peroxide by titration with potassium permanganate is not applicable with accuracy to the determination of the peroxide present in solutions of permonosulphuric acid on account of the acid reacting with the hydrogen peroxide under the conditions existing during the titration with the formation of free oxygen, the permanganate titration therefore giving low results.⁴

Silver nitrate causes vigorous decomposition of a neutralised solution of permonosulphuric acid, ozonised oxygen being rapidly evolved; manganese dioxide and lead dioxide produce a similar effect.⁵

¹ d'Ans and Friederich, *Zeitsch. anorg. Chem.*, 1911, 73, 325; also d'Ans, *Zeitsch. Elektrochem.*, 1911, 17, 849.

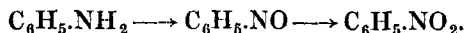
² Baeyer and Villiger, *Ber.*, 1901, 34, 853. See also Price, *Trans. Chem. Soc.*, 1907, 91, 535.

³ Price, *Trans. Chem. Soc.*, 1903, 83, 543; Price and Friend, *ibid.*, 1904, 85, 1526.

⁴ Price, *Trans. Chem. Soc.*, 1903, 83, 543. The fact that on titration of hydrogen peroxide with permanganate in the presence of permonosulphuric acid an apparently excessive quantity of oxygen is liberated was earlier the subject of considerable controversy; see Bach, *Ber.*, 1900, 33, 1506, 3111; 1901, 34, 1520, 3851; 1902, 35, 158, 872, 3940; Baeyer and Villiger, *ibid.*, 1900, 33, 2488; Armstrong, *Proc. Chem. Soc.*, 1900, 16, 134; Ramsay, *Trans. Chem. Soc.*, 1901, 79, 1324.

⁵ Bamberger, *Ber.*, 1900, 33, 1959.

Oxidising Action.—The most characteristic property of permonosulphuric acid is its oxidising power, in which it is distinctly superior to perdisulphuric acid. Chlorides, bromides and iodides are oxidised, the last-named immediately, with liberation of the corresponding halogen element. Many organic compounds undergo oxidation with the acid, and it has found extended application in this direction. Particularly noteworthy is its action on aromatic amines; aniline, for example, is rapidly converted through the stage of nitrosobenzene to nitrobenzene:



The formation of aniline black as with perdisulphuric acid (p. 186) is not observed.¹

For use as an oxidising agent the addition of potassium permanganate to a dilute sulphuric acid solution of permonosulphuric acid has been recommended.²

Constitution.—On account of the fact that pure permonosulphuric acid and permonosulphates were unobtainable, the selection of a formula for permonosulphuric acid was at one time a matter of considerable difficulty. It was recognised that the acid must be derived from sulphuric acid, but the actual composition was in doubt for a considerable period. Baeyer and Villiger³ proposed the formula H_2SO_5 , but rival formulæ were also put forward, namely $\text{H}_2\text{S}_4\text{O}_{14}$,⁴ and $\text{H}_2\text{S}_2\text{O}_9$,⁵ and advocated strongly. Convincing evidence of the correctness of the first formula was first adduced by Willstätter and Hauenstein,⁶ who treated a neutralised solution of the acid with benzoyl chloride and alkali and so obtained a crystalline *benzoyl derivative*, which could be purified by careful crystallisation from water; this product, after drying in a vacuum, proved to have the composition $\text{KO}\cdot\text{SO}_2\cdot\text{O}\cdot\text{OBz}$ (where Bz represents the benzoyl radical, $\text{C}_7\text{H}_5\text{O}$), but immediately after separation from water contained a molecule of water of crystallisation. The benzoyl derivative possessed oxidising properties, as would be expected of a substance of the peroxidic type suggested, and its composition finally disposed of any probability attaching to the alternative formulæ for permonosulphuric acid. The synthesis of pure permonosulphuric acid by sulphonating hydrogen peroxide with the calculated quantity of chlorosulphonic acid⁷ removed any remaining shadow of doubt on the matter.

It must be borne in mind that of the hydrogen atoms of permonosulphuric acid, $\text{HO}\cdot\text{SO}_2\cdot\text{O}\cdot\text{OH}$, only that of the simple hydroxyl group is acidic, the substance being a monobasic acid; it is possible that the hydrogen of the $-\text{O}_2\text{H}$ group may become active in the presence of a

¹ Caro, *Zeitsch. angew. Chem.*, 1898, 11, 845.

² Baeyer and Villiger, *Ber.*, 1900, 33, 2488. For the further application of permonosulphuric acid to organic processes, see Baeyer and Villiger, *Ber.*, 1899, 32, 3625; 1900, 33, 124, 854, 2479; Bamberger and others, *ibid.*, 1899, 32, 1676; 1900, 33, 533, 1781; 1901, 34, 2023; 1902, 35, 1082; Cross, Bevan and Briggs, *Chem. News*, 1900, 82, 163; Wolfenstein and others, *Ber.*, 1899, 32, 432; 1901, 34, 2423; 1904, 37, 3215, 3221; etc.

³ Baeyer and Villiger, *Ber.*, 1900, 33, 124; 1901, 34, 853.

⁴ Lowry and West, *Trans. Chem. Soc.*, 1900, 77, 950.

⁵ Armstrong and Lowry, *Proc. Roy. Soc.*, 1902, 70, 94; Mugdan, *Zeitsch. Elektrochem.*, 1903, 9, 719.

⁶ Willstätter and Hauenstein, *Ber.*, 1909, 42, 1839; Price (*Trans. Chem. Soc.*, 1903, 83, 543; 1906, 89, 54) had already obtained less convincing evidence in favour of the same formula.

⁷ d'Ans and Friederich, *Ber.*, 1910, 43, 1880. See also this volume, p. 189.

large excess of alkali, the acid becoming somewhat more stable under such conditions.¹

Detection and Estimation.—Pure solutions of permonosulphuric acid give no yellow coloration with a solution of titanium dioxide in sulphuric acid and so may be distinguished from similar solutions owing their oxidising power to the presence of hydrogen peroxide.

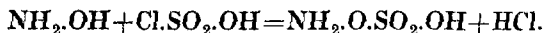
Quantitative estimation of the acid may be effected by the use of potassium iodide solution, the chemical change



being capable of examination both from the point of view of the liberation of iodine and decrease in acidity.² The estimation should be carried out in the cold and as rapidly as possible.

Amidopermonosulphuric Acid or Hydroxylamineisosphonic Acid, $\text{NH}_2\cdot\text{O}\cdot\text{SO}_2\cdot\text{OH}$.

When hydroxylamine is made to react with chlorosulphonic acid at the ordinary temperature, the hydroxyl group of the former undergoes sulphonation,³ as represented in the equation :



The same substance can also be obtained from hydroxylamine sulphate and fuming sulphuric acid, and by the hydrolysis of hydroxylamineisodisulphonic acid with hydrochloric acid.⁴

The product is a microcrystalline powder which can be hydrolysed to hydroxylamine by heating in acid solution.

As will be seen by comparing the formulæ of sulphuric acid, $\text{SO}_2(\text{OH})_2$, and sulphamide, $\text{SO}_2(\text{NH}_2)_2$, hydroxylamineisosphonic acid is the amide corresponding with permonosulphuric acid, although it has not been directly prepared from this acid. In agreement with this relationship, however, hydroxylamineisosphonic acid or amidopermonosulphuric acid possesses marked oxidising properties, readily liberating iodine from potassium iodide.

Thiosulphuric Acid, $\text{H}_2\text{S}_2\text{O}_3$.

Sodium thiosulphate was obtained probably for the first time by Chaussier in 1799 when endeavouring to prepare sodium carbonate by heating sodium sulphate with charcoal. The name hyposulphurous acid for the corresponding acid was suggested by Gay-Lussac in 1818,⁵ who wrongly regarded the acid as representing an intermediate stage of oxidation between sulphur and sulphurous acid. In 1877 Wagner recommended the more correct description "thiosulphuric acid,"⁶ which has almost entirely displaced the earlier name from chemical literature, although "hyposulphite" is still used by photographers.

¹ Willstätter and Hauenstein, *loc. cit.*

² See Mugdan, *Zeitsch. Elektrochem.*, 1903, 9, 718, 980; Price, *Trans. Chem. Soc.*, 1903, 83, 543. For a method of estimating Caro's acid, perdisulphuric acid and hydrogen peroxide in a mixture of all three, see Wolfenstein and Makow, *Ber.*, 1923, 56, [B], 1768.

³ Sommer and Templin, *Ber.*, 1914, 47, 1221.

⁴ Raschig, *Annalen*, 1887, 241, 161.

⁵ Gay-Lussac, *Ann. Chim.*, 1813, 85, 191.

⁶ Wagner, *Dingl. poly. J.*, 1877, 225, 383.

Formation.—The free acid is exceedingly unstable and, at best, is obtainable only in very dilute solution; many of the older methods described for the synthetic production of aqueous solutions of the acid probably yielded only one or more of the polythionic acids.¹

Under suitable conditions, however, sulphurous acid appears to be capable of combining directly with sulphur, giving some thiosulphuric acid, the conditions being most favourable in alcohol solution² at the ordinary temperature.

A more satisfactory method is to pass dry hydrogen sulphide into alcohol containing lead thiosulphate in suspension; after filtering off the lead sulphide formed, excess of hydrogen sulphide is removed from the solution by a current of air.³ The solution obtained decomposes in the course of a few days.

The acid appears to be formed when a few drops of a concentrated solution of sodium thiosulphate are added to a few cubic centimetres of fuming hydrochloric acid. Sodium chloride is precipitated and a clear solution obtained which remains stable for about an hour.⁴

The salts are much more stable and can be prepared by various processes; the sodium salt is the one most commonly manufactured.

Sulphites of the alkali metals when heated in aqueous solution with sulphur or polysulphides are converted into thiosulphates; the sulphur should be in excess and the mixture kept well stirred.⁵ A similar conversion can be effected by careful heating in the absence of a solvent,⁶



A similar result is achieved by treating an alkali sulphite in aqueous solution with hydrogen sulphide, the formation of sulphur probably occurring as the first stage⁷ (see p. 194).

The interaction of aqueous alkalis and sulphur (see p. 37), and of fused alkalis or alkali carbonates with the same element, also produces some thiosulphate.

Alkali sulphides⁸ and polysulphides⁹ on suitable oxidation give rise to thiosulphates; the formation of thiosulphate by the action of sulphur dioxide¹⁰ on an alkali sulphide may be considered as a special case of this class or a modification of the method given first above. If aqueous solutions of sodium hydrogen sulphide and sodium hydrogen

¹ For example, see Rose, *Zeitsch. anal. Chem.*, 1862, 1, 475; Myers, *Compt. rend.*, 1872, 74, 195; Debus, *Annalen*, 1888, 244, 79; Colefax, *Trans. Chem. Soc.*, 1892, 61, 199.

² Aloy, *Compt. rend.*, 1903, 137, 51.

³ Gil and Beato, *Ber.*, 1923, 56, [B], 2451; *Anal. Fis. Quim.*, 1924, 22, 84.

⁴ Gil and Beato, *loc. cit.*

⁵ Watson and Rajagopalan, *J. Indian Inst. Sci.*, 1925, 8, A, 275. See also Hargreaves and Dunningham, *J. Soc. Chem. Ind.*, 1923, 42, 147 T.

⁶ Verein Chem. Fabriken, *Zeitsch. angew. Chem.*, 1896, 9, 666. The reaction $\text{S} + \text{CaSO}_3 \cdot 2\text{H}_2\text{O} = \text{CaS}_2\text{O}_3 \cdot \text{aq.} + 2\text{H}_2\text{O}$ has been subjected to thermodynamic investigation by Bichowsky, *J. Amer. Chem. Soc.*, 1923, 45, 2225.

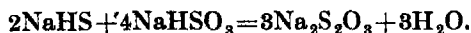
⁷ Mitscherlich, *Ann. Phys. Chem.*, 1826, [ii.], 8, 441.

⁸ Donath and Müllner, *Dingl. poly. J.*, 1887, 263, 211; 1888, 267, 143.

⁹ Jones, *Trans. Chem. Soc.*, 1880, 37, 461; Colson, *Bull. Soc. chim.*, 1880, 34, 66; Drechsel, *J. prakt. Chem.*, 1871, [ii.], 4, 20; Senderens, *Bull. Soc. chim.*, 1891, [iii.], 6, 800; 1892, [iii.], 7, 511.

¹⁰ Drechsel, *J. prakt. Chem.*, 1872, [ii.], 5, 367; Divers and Shimidzu, *Trans. Chem. Soc.*, 1884, 45, 270.

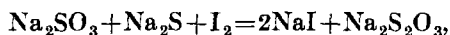
sulphite in the molecular proportion 1 : 2 are mixed, sodium thiosulphate is obtained in a high degree of purity : ¹



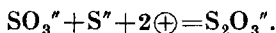
Also, in the preparation of the thiosulphate from sodium sulphide and sulphur dioxide, or from sodium sulphite and hydrogen sulphide, as already described, if sodium hydroxide is first added to the solution in such quantity as to lead to the ultimate formation of the hydrogen sulphide and hydrogen sulphite salts in the proportions mentioned, then the reaction proceeds very smoothly and almost without separation of sulphur.

The decomposition of the polythionic acids (*q.v.*) in the presence of alkali, the decomposition of hydrosulphites (p. 227) and the hydrolysis of nitrogen sulphide ² by water or aqueous alkali are also processes in which salts of thiosulphuric acid are formed. Certain micro-organisms capable of converting sulphur to thiosulphate have been isolated from soil cultures. ³

Of especial interest from the point of view of the molecular constitution of the thiosulphates, is the possibility of preparing the alkali salts from the corresponding sulphites and sulphides by the action of iodine : ⁴



or by electrolysis, in which case thiosulphate is produced at the anode : ⁵



For details of the commercial processes for the manufacture of thiosulphates, the volumes of this series dealing with the particular salts in question should be consulted.

Properties.—As is to be expected from its unstable nature, thiosulphuric acid is endothermic when referred to aqueous sulphur dioxide and free sulphur or even to sulphur dioxide, water and sulphur, although, on account of the high value of the heat of formation of water, the heat of formation of the acid from its elements is a positive quantity, amounting to 137.83 Calories per gram-molecule in aqueous solution. ⁶

When solutions of the salts are acidified there is a gradual deposition of sulphur, the rate being dependent on the concentration of the solutions as well as on other factors. No turbidity is observable at first, and the interval is sometimes ascribed to the sulphur remaining in colloidal solution for a time, ⁷ subsequent neutralisation not preventing the later separation of at least some of the sulphur; also, the presence of colloidal particles may be detected by the ultra-microscope. ⁸ With solutions of one gram-molecule of sodium thiosulphate and one gram-molecule of

¹ Foerster and Mommsen, *Ber.*, 1924, 57, [B], 258.

² Fordos and Gélis, *Compt. rend.*, 1850, 31, 702; Ruff and Geisel, *Ber.*, 1904, 37, 1573. See also p. 234.

³ Guittonneau, *Compt. rend.*, 1925, 180, 1142.

⁴ Spring, *Ber.*, 1874, 7, 1159.

⁵ Levi and Voghera, *Atti R. Accad. Lincei*, 1905, [v.], 14, ii., 433; 1906, [v.], 15, i., 322, 363.

⁶ Thomsen, *Ber.*, 1873, 6, 1535; Berthelot, *Compt. rend.*, 1889, 108, 776.

⁷ Holleman, *Rec. Trav. chim.*, 1895, 14, 71; *Zeitsch. physikal. Chem.*, 1900, 33, 500; von Ottingen, *ibid.*, 1900, 33, 1.

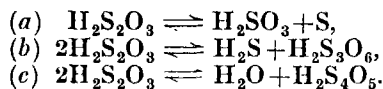
⁸ Biltz and Gahl, *Nachr. K. Ges. Wiss. Göttingen*, 1904, p. 300.

hydrochloric acid, each in 16 litres of water at 12° C., a mixture of equal volumes gives no turbidity until after one and a half minutes.¹

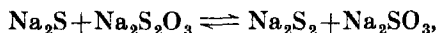
The foregoing view of the cause of the delayed turbidity is correct only in part, considerable evidence pointing to at least a definite although short existence of thiosulphuric acid itself; for instance, the decomposition of thiosulphuric acid is a slightly reversible process (see p. 193); also, sodium thiosulphate can be titrated satisfactorily with iodine in dilute acid solution, and an acidified solution of a thiosulphate will reduce Methylene Blue in aqueous alcohol solution, whereas sulphurous acid will not.² During the decomposition of the thiosulphuric acid, however, secondary reactions occur, resulting in the formation of polythionic acids, and considerable investigation has been directed towards this subject in recent years, the main conclusions from which will now be given.

Decomposition of Thiosulphuric Acid.

Aqueous solutions of thiosulphuric acid and its salts are not very stable, but tend to decompose, yielding sulphurous and polythionic acids and a deposit of sulphur. The decomposition may take place in at least three different ways :³



Of these, the first reaction is the one usually recorded, and in the majority of cases it is the one that occurs to the largest extent. The presence of alkali pushes the equilibrium well to the left, so that in alkaline solution the thiosulphate is stable. This explains the formation of thiosulphates on boiling alkaline sulphite solutions with sulphur. The laws of chemical equilibria, however, demand the presence of perfectly definite although perhaps very small quantities of sulphite and free sulphur in solution, and if alkaline thiosulphate solutions containing alkali sulphide are boiled in the absence of air, they become deep yellow, owing to polysulphide formation, the extra sulphur for which is obtained from the thiosulphate. Assuming the sodium derivatives to be used, the equation may be written



and higher polysulphides may result as well.

This equilibrium affords an explanation for the fact that a trace of hydrogen sulphide accelerates the reaction between sodium sulphite and sulphur; ⁴ sometimes there is a long delay before sulphur begins to dissolve in boiling sodium sulphite solution, and in such cases the effect of passing a few bubbles of hydrogen sulphide into the solution is very marked; when once the reaction begins it proceeds smoothly.⁵

Although the reaction (a) is usually written in the manner indicated

¹ Muller, *Bull. Soc. chim.*, 1907, [iv.], 1, 1155.

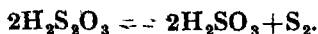
² Bongiovanni, *Gazzetta*, 1914, 44, i., 624.

³ Bassett and Durrant, *J. Chem. Soc.*, 1927, p. 1416.

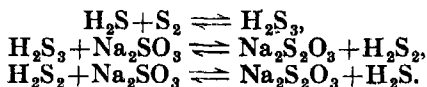
⁴ Hargreaves and Dunningham, *J. Soc. Chem. Ind.*, 1923, 42, 147 T; Watson and Rajagopalan, *J. Indian Inst. Sci.*, 1925, 8, A, 275.

⁵ Bassett and Durrant, *loc. cit.*

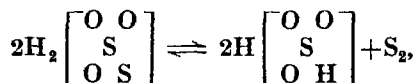
it appears to be bimolecular, and may be more correctly represented as ¹



This seems to suggest that the sulphur unit is S_2 . This unit is capable of uniting with hydrogen sulphide to form the trisulphide, H_2S_3 ; but sodium sulphite can only combine with one atom of sulphur to yield thiosulphate. The catalytic activity of the hydrogen sulphide would thus appear to be due to its ability to absorb a whole sulphur unit, S_2 , and subsequently to give up, on reduction, each atom of sulphur separately, thus :



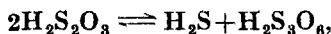
The manner in which the S_2 unit is eliminated from thiosulphuric acid remains to be considered. Bassett and Durrant point out that when the known weakness of the second stage ionisation of sulphurous acid is considered in conjunction with the known tendency for sulphur to become co-ordinated with four atoms or groups, it would appear that the direct loss of sulphur by thiosulphuric acid is largely due to a hydrogen atom taking the place of the escaping sulphur atom, thus :



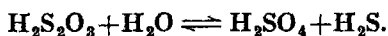
the sulphurous acid produced having, in the first instance at any rate, the sulphonic structure.

From spectrophotometric measurements, Jabłoński and Rytel,² however, maintain that the decomposition is unimolecular, monatomic sulphur being first produced, which itself retards the reaction. As the opalescence is due to the formation of polyatomic sulphur aggregates, the latter act as an autocatalyst by withdrawing the atomic sulphur from the solution.

Turning now to equation (b), namely



it has been known for many years that, upon acidification, solutions of thiosulphates invariably evolve hydrogen sulphide.³ Water alone suffices to cause evolution of the gas from sodium thiosulphate. The gas is evolved also if carbon dioxide is bubbled through the solutions, or if the thiosulphate is warmed with boric acid, whilst stronger acids liberate it readily.⁴ Various explanations have been offered for this, some attributing the presence of the gas in standard sodium thiosulphate solution to bacterial action (see p. 199), whilst Foerster and his co-workers⁵ suggest hydrolysis, according to the equation



¹ Bassett and Durrant, *loc. cit.*; contrast Holleman, *Rec. Trav. chim.*, 1895, 14, 71.

² Jabłoński and Rytel, *Rocz. Chem.*, 1926, 6, 201; *Bull. Soc. chim.*, 1926, [iv.], 39, 409.

³ Spring and Levy, *Bull. Acad. roy. Belg.*, 1876, 42, 103; Colson, *Bull. Soc. chim.*, 1880, 34, 66.

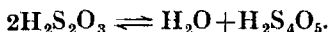
⁴ Bassett and Durrant, *loc. cit.*

⁵ Foerster, Lange, Drossbach and Seidel, *Zeitsch. anorg. Chem.*, 1923, 128, 268.

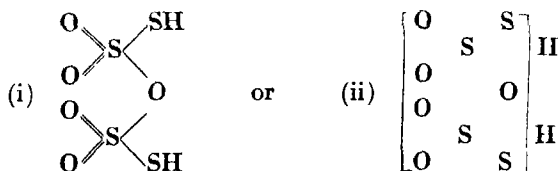
Against this latter view is the fact that little or no sulphuric acid is formed unless the mixture is boiled for a long time. In alkaline solution, alkali sulphide and trithionate react to form thiosulphate,¹ but alkaline solutions of sulphate and sulphide do not.² It would appear, therefore, that the correct explanation lies in the reversible equation (b) (p. 195). This receives support from the fact that when lead thiosulphate is boiled with water it yields, in the first instance, lead sulphide and lead trithionate.³ Conversely, lead sulphide on digestion with potassium trithionate yields lead thiosulphate.⁴ Further, weakly alkaline solutions of sodium thiosulphate itself yield, on boiling, sodium sulphide and sodium trithionate, with only a trace of sulphate; if boiled with sodium plumbite, lead sulphide is precipitated and sodium trithionate remains in solution.

When acids act on thiosulphates, polythionic acids are formed.⁵ This is explained by reactions (b) and (c). The fact that the amount of hydrogen sulphide liberated is very small in proportion to the amount of polythionic acid formed is attributed⁶ to the fact that reaction (a) is that which normally occurs to the greatest extent when acid acts upon thiosulphate; the hydrogen sulphide is thus liberated in the presence of a large amount of sulphurous acid and hence rapidly destroyed. Trithionic acid is thus a primary product of thiosulphate decomposition, and in its turn decomposes as explained on p. 212.

In very acid solution, Bassett and Durrant believe that reaction (c) takes place, with formation of a new acid, **di-thio-pyrosulphuric acid**, $\text{H}_2\text{S}_4\text{O}_5$:



This reaction is clearly effective in removing hydrogen ions from solution. The acid is presumed to be formed by the removal of a molecule of water from two hydroxyl groups of two molecules of thiosulphuric acid—not from one hydroxyl and one thiol group—in which case its structure may be written as:



From the second formula it is clear that three tautomeric structures are possible, according as both hydrogen atoms are ionisable (as in the formula), or one or both atoms are absorbed into the complex, being attached by co-valencies to either a sulphur or an oxygen atom.

When ice-cold concentrated hydrochloric acid is added to a thio-sulphate solution, a colourless solution is obtained similar to that resulting from the action of sulphur dioxide (see p. 198), no sulphur

¹ Chancel and Diacon, *Compt. rend.*, 1863, 56, 710; *J. prakt. Chem.*, 1863, 90, 55.

² Bassett and Durrant, *loc. cit.*

³ Fogh, *Compt. rend.*, 1890, 110, 524.

⁴ Spring, *Bull. Acad. roy. Belg.*, 1874, 37, 45; *Collected Researches*, 1923, vol. ii., p. 966.

⁵ Chancel and Diacon, *loc. cit.*

⁶ Bassett and Durrant, *loc. cit.*

being precipitated. After fifteen hours no thiosulphate can be detected in the solution.

Although the foregoing explanation may be valid, it has been suggested¹ that the compound formed in solution is of the type $\text{H}_2\text{S}_2\text{O}_3 \cdot \text{SO}_2$.

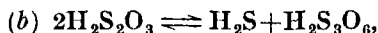
Sulphurous acid causes the decomposition of thiosulphuric acid to take place more in accordance with equation (b);² this it does in three ways, namely:

(i) By retarding reaction (a), of which it is a product:

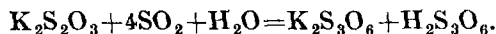


(ii) by forming a relatively stable additive product, $\text{H}_2\text{S}_2\text{O}_3 \cdot \text{SO}_2$;

(iii) by accelerating reaction (b):



through removal of hydrogen sulphide, with which it interacts, liberating sulphur, which may, under favourable conditions, react with more sulphurous acid to regenerate thiosulphuric acid. It is thus possible to convert a thiosulphate almost quantitatively into trithionate, as, for example, by acting upon a saturated solution of the potassium salt with concentrated sulphurous acid at 30°C .³ thus:



The reaction, of course, will not end there: continued action of sulphurous acid results in the hydrolysis of the trithionate, with formation of tetra- and penta-thionates, and ultimately of sulphate and sulphur.⁴

If gaseous sulphur dioxide is passed into a solution of thiosulphate, a yellow solution is formed which on keeping becomes colourless; it then yields a precipitate of sulphur when treated with formaldehyde and sodium hydroxide, but no polythionate can be detected. When the colourless solution is neutralised with sodium hydroxide, it is found to contain sulphite and thiosulphate, but sulphur is not precipitated. These results may be due to the formation of an additive compound such as that mentioned in (ii) above.⁵

Free thiosulphuric acid solutions are rendered more stable by the addition of alcohol;⁶ decomposition is facilitated by exposure to direct sunlight,⁷ and its course is dependent on the conditions prevailing at the time. Thus, acids generally accelerate the decomposition, as also do charcoal⁸ and finely divided (colloidal) sulphur⁹ in the presence of

¹ Kurtenacker and Czernotzky, *Zeitsch. anorg. Chem.*, 1928, 175, 231.

² Bassett and Durrant, *J. Chem. Soc.*, 1927, p. 1440; Foerster and Vogel, *Zeitsch. anorg. Chem.*, 1926, 155, 161.

³ Hertlein, *Zeitsch. physikal. Chem.*, 1896, 19, 292.

⁴ For earlier views concerning the action of sulphurous acid on thiosulphates, see Baker, *Chem. News*, 1877, 36, 203; Debus, *Annalen*, 1888, 244, 169; Berthelot, *Compt. rend.*, 1889, 108, 971; Vilhers, *ibid.*, 1888, 106, 851; 1889, 108, 402; Colefax, *Chem. News*, 1892, 65, 48; *Trans. Chem. Soc.*, 1892, 61, 1083; Holleman, *Rec. Trav. chim.*, 1895, 1, 71; Hertlein, *Zeitsch. physikal. Chem.*, 1896, 19, 291. For a study of the reaction between ammonium thiosulphate, ammonium polythionates, sulphur dioxide and ammonium see Espenhahn, *J. Soc. Chem. Ind.*, 1917, 36, 483.

⁵ See Kurtenacker and Czernotzky, *Zeitsch. anorg. Chem.*, 1928, 175, 231.

⁶ Aloy, *Compt. rend.*, 1903, 137, 51; Landolt, *Ber.*, 1883, 16, 2967.

⁷ Aloy, *loc. cit.*; Kolthoff, *Pharm. Weekblad*, 1919, 56, 878. See also Mayr and Kers, *34. Ann. Zeitsch. anal. Chem.*, 1928, 73, 321.

⁸ Kolthoff, *Rec. Trav. chim.*, 1920, 48, 298.

⁹ Foerlezyński and Frenkenberg, *Bull. Soc. chim.*, 1929, [iv.], 45, 210.

acid. Many salts retard the change,¹ although some, such as mercuric and bismuth chlorides, lead acetate, sodium tungstate and sulphide, have no marked influence² on the decomposition of the sodium salt by means of hydrochloric acid. Protective colloids also retard the reaction.³ The presence of alkaline substances has a stabilising effect, and the addition of sodium carbonate (about 0.2 gram per litre) to standard volumetric solutions of sodium thiosulphate will preserve them for a considerable time.⁴ Such solutions should be made with boiled distilled water in order to minimise the decomposing action attributed to bacteria.⁵

According to Mayr and Kerschbaum⁶ bacterial action is the principal cause of the instability of thiosulphate solutions, and the protective action of alkali is ascribed to its restraining effect on the growth of the bacteria, a p_H value of 9 to 10 being most effective. The presence of copper accelerates decomposition only when bacteria are also present. Thiosulphate solutions may be almost completely sterilised by the addition of amyl alcohol (1 per cent. by volume) or of mercuric cyanide (0.01 per cent. by weight).⁷

The addition of formaldehyde to sodium thiosulphate solution prevents its decomposition with precipitation of sulphur on subsequent addition of hydrochloric acid; this effect is to be attributed to the formation of a condensation product analogous to that formed between formaldehyde and sodium hydrogen sulphite.⁸

From the fact that sodium thiosulphate is but slightly affected by acetic acid, it is probable that thiosulphuric acid is a comparatively strong acid.⁹

Thiosulphates.—The salts of thiosulphuric acid, with the exception of those of the alkali metals, are sparingly soluble in water but are commonly much more soluble in an aqueous solution of an alkali thiosulphate, soluble double salts being formed in which the heavier metal is probably situated in a complex acidic radical; hence, on the addition of a solution of alkali thiosulphate to a salt of a heavy metal, the precipitate of the thiosulphate of the metal is generally soluble in excess.

The formation of these relatively stable complex salts explains the solubility of the silver halides in sodium thiosulphate solution and the value of such a solution for "fixing" photographic prints. In many cases the complex salts have been isolated in the solid state,¹⁰ for example,

¹ Gaillard, *Compt. rend.*, 1905, **140**, 652.

² Kurtenacker and Czernotzky, *Zeitsch. anorg. Chem.*, 1928, **175**, 367. See this paper also for the influence of arsenic compounds on the reaction, also this volume, p. 217.

³ Jablczynski and Rytel, *Bull. Soc. chim*, 1926, [iv.], **39**, 409.

⁴ Kolthoff, *Pharm. Weekblad*, 1919, **56**, 878.

⁵ See Kilpatrick and Kilpatrick, *J. Amer. Chem. Soc.*, 1923, **45**, 2132; Feigl, *Ber.*, 1923, **56**, [B], 2086; Abel, *ibid.*, p. 1076; Skrabal, *Zeitsch. anal. Chem.*, 1924, **64**, 107; Schulek, *ibid.*, 1926, **68**, 387; Mayr, *ibid.*, p. 274; Hahn, *ibid.*, p. 386.

⁶ Mayr and Kerschbaum, *Zeitsch. anal. Chem.*, 1928, **73**, 321.

⁷ Winkler, *Pharm. Zentr.*, 1928, **69**, 360.

⁸ Schmidt, *Ber.*, 1906, **39**, 2413; 1907, **40**, 865.

⁹ Mattheu-Plessy, *Compt. rend.*, 1885, **101**, 59; Berthelot, *ibid.*, 1889, **108**, 971.

¹⁰ See under the various metals in other volumes of this Series. Also see Vortmann, *Monatsh.*, 1888, **9**, 165; Vortmann and Padberg, *Ber.*, 1889, **22**, 2637; Fock and Klüss, *ibid.*, 1891, **24**, 1351, 3016; Rosenheim and Steinhäuser, *Zeitsch. anorg. Chem.*, 1900, **25**, 81; Shunn, *J. Amer. Chem. Soc.*, 1904, **26**, 947; Meyer and Eggeling, *Ber.*, 1907, **40**, 351; Dutoit, *J. Chim. phys.*, 1913, **11**, 650; Vanino and Mussnug, *Arch. Pharm.*, 1919, **257**, 264; von Szilágyi, *Zeitsch. anorg. Chem.*, 1920, **113**, 69, 75; Cannieri and Luchini, *Gazzetta*, 1922, **52**, ii, 261; Bassett and Durrant, *Trans. Chem. Soc.*, 1923, **123**, 1279.

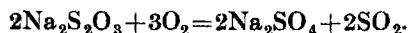
from solutions containing sodium thiosulphate and a silver salt, well-defined crystalline compounds variously formulated as $\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Ag}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, $2\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Ag}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Ag}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$, have been obtained. According to Baines¹ the first of these may best be obtained in a pure condition by the addition of silver carbonate in aqueous suspension to a solution of sodium thiosulphate, when the double salt separates as a colourless crystalline powder; or it may be obtained in larger crystals by saturating with sulphur dioxide a dilute solution of silver carbonate and sodium sulphite in aqueous sodium thiosulphate. According to the same investigator the salt should be considered as sodium monoargentomonothiosulphate, $\text{Na}[\text{AgS}_2\text{O}_3] \cdot \text{H}_2\text{O}$. When pure it darkens only very slightly in bright light, and in solution it is more stable than sodium thiosulphate towards dilute acids. The free acid, monoargentomonothiosulphuric acid, $\text{H}[\text{AgS}_2\text{O}_3] \cdot \text{H}_2\text{O}$, may be obtained as a silky white precipitate by the addition of concentrated nitric acid to the sodium double salt in ammoniacal solution. It is less stable than the salt. A solution of the latter precipitated with alcohol yields a salt of composition $\text{Na}_3[\text{Ag}_3(\text{S}_2\text{O}_3)_4] \cdot 2\text{H}_2\text{O}$, and there is evidence that a third salt, $\text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2]$, exists in solution.

Many of the heavier thiosulphates when heated with water give rise to the corresponding sulphides.² To this ready decomposition of the thiosulphate is due the precipitation of sulphides when hot acid-containing solutions of various metals are treated with sodium thiosulphate solution.³ When a solution of alkali thiosulphate is boiled with a copper salt, the yellow precipitate of sodium cuprous thiosulphate first formed undergoes decomposition to produce cuprous and cupric sulphides and free sulphur, the relative amounts of these products depending on the thiosulphate concentration, the duration of boiling, and the acidity of the solution.⁴

When heated strongly with exclusion of air, thiosulphates undergo decomposition, giving sulphate and polysulphide or the further decomposition products of the latter, namely, sulphide and free sulphur:⁵



When heated in the presence of air, slow oxidation to sulphate and sulphur dioxide occurs:⁶



In the presence of a reducing agent, for instance hydrogen, carbon or sulphur, the corresponding sulphide may be the almost exclusive product. A similar reduction to sulphide may be effected in aqueous

¹ Baines, *J. Chem. Soc.*, 1920, p. 2763; *Phot. J.*, 1920, 53, 314.

² Fleck, *J. prakt. Chem.*, 1866, 99, 247; Vortmann, *Ber.*, 1889, 22, 2309; Norton, *Chem. News*, 1901, 89, 254; Fogh, *Ann. Chim. Phys.*, 1890, [vi.], 21, 56; Faktor, *Zeitsch. anal. Chem.*, 1900, 39, 351. The conversion into sulphide is far from complete in the case of lead thiosulphate, see Perkins and King, *Trans. Chem. Soc.*, 1913, 103, 300; also this volume, p. 204.

³ Lea, *Amer. J. Sci.*, 1867, [n.], 44, 222; Geuther, *Annalen*, 1884, 226, 232; Vaubel, *Ber.*, 1889, 22, 1692; Faktor, *Pharm. Post.*, 1905, 38, 219, 527, 539.

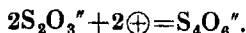
⁴ Hanuš and Hovorka, *J. Czechoslov. Chem. Comm.*, 1929, 1, 65.

⁵ Rammelsberg, *Ann. Phys. Chem.*, 1842, [n.], 56, 298; Berthelot, *Compt. rend.*, 1883, 96, 146; Jacques, *Chem. News*, 1903, 88, 295; Picon, *Compt. rend.*, 1924, 178, 1548.

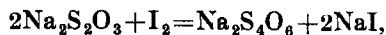
⁶ Picon, *loc. cit.*

solution with nascent hydrogen,¹ or even by *in situ* fermentation of sugar with yeast.²

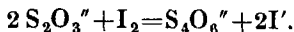
Electrolysis of a thiosulphate in neutral solution causes the formation of tetrathionate at the anode :³



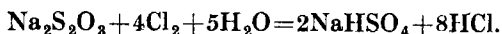
A similar effect is produced by treatment with iodine,⁴ but in the presence of alkali there is also some sulphate⁵ formed :



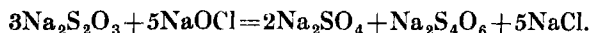
or in ionic terms :



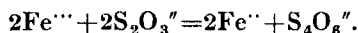
Chlorine and bromine exert a more vigorous oxidising action than iodine, and although some tetrathionate may be formed, this is accompanied by much sulphate, the latter being the main product :⁶



With sodium hypochlorite in the presence of acid, or even in the presence of sodium hydrogen carbonate, the reaction proceeds according to the foregoing equation, but if the thiosulphate and hypochlorite are allowed to react in dilute solution, the course followed is according to the equation :⁷



As might be expected, treatment with vigorous oxidising agents such as nitric acid or permanganic acid, converts a thiosulphate into a sulphate and sulphuric acid (or an acid sulphate).⁸ A mixture of alkali thiosulphate and nitrate heated in a dry tube is liable to explode. With milder oxidising agents, for example iodic acid⁹ or ferric chloride,¹⁰ intermediate products are obtainable, especially tetrathionate, and sometimes dithionate. The oxidation of sodium thiosulphate by a solution of iron alum is of interest as presenting an example of a quadrimolecular reaction :¹¹



In alkaline solution hydrogen peroxide effects oxidation to sulphate, dithionate being a probable intermediate product ; sulphate is also

¹ Vohl, *Annalen*, 1855, 96, 237 ; Reynolds, *Chem. News*, 1863, 8, 283 ; Spring, *Ber.*, 1874, 7, 1161 ; de Koninck, *ibid.*, 1887, 20, 397.

² Neuberg and Welde, *Biochem. Zeitsch.*, 1914, 67, 111.

³ Thatcher, *Zeitsch. physikal. Chem.*, 1904, 47, 691.

⁴ Hertlein, *ibid.*, 1896, 19, 310.

⁵ Ashley, *Amer. J. Sci.*, 1904, [iv.], 19, 237. See also Pickering, *Trans. Chem. Soc.*, 1880, 37, 128 ; Kolthoff, *Pharm. Weekblad*, 1919, 56, 572.

⁶ Lunge, *Ber.*, 1879, 12, 404 ; Berthelot, *Compt. rend.*, 1888, 106, 773, 925, 971.

⁷ Diénert and Wandenbulcke, *Compt. rend.*, 1919, 169, 29.

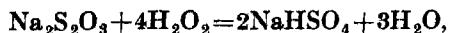
⁸ Slater, *Chem. Gaz.*, 1855, p. 369 ; Longi, *Gazzetta*, 1896, 26, ii., 119 ; Feit and Kubierschky, *Chem. Zeit.*, 1891, p. 351 ; Stingl and Morawski, *Ber.*, 1885, 18, 372 ; Hönic and Zatzek, *ibid.*, 1883, 16, 2660 ; 1886, 19, 229 ; Glaser, *ibid.*, 1887, 20, 116 ; Brügelmann, *ibid.*, 1884, 17, 65 ; Luckow, *Zeitsch. anal. Chem.*, 1893, 32, 53. For the action of nitric oxide on certain thiosulphates with formation of nitrosothiosulphates, see Cambi and Clerici, *Atti R. Accad. Lincei*, 1927, [vi.], 6, 448.

⁹ Sonstadt, *Chem. News*, 1872, 26, 98 ; Walker, *Amer. J. Sci.*, 1897, [iv.], 4, 235.

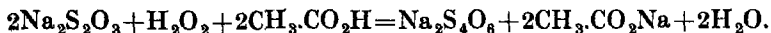
¹⁰ Popp, *Zeitsch. Chem.*, 1870, [ii.], 6, 330 ; Holluta and Martini, *Zeitsch. anorg. Chem.*, 1924, 140, 206 ; 141, 23 ; 1925, 144, 321.

¹¹ Hewitt and Mann, *Trans. Chem. Soc.*, 1913, 103, 324.

obtained with hydrogen peroxide in the presence of molybdic acid as catalyst :

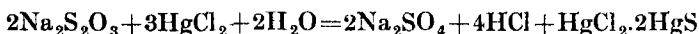


but in the presence of alkali the peroxide produces trithionate (see p. 210), whilst in the presence of a feeble acid like acetic acid the product is tetrathionate; iodine catalytically accelerates the last change :¹



Applications of the Thiosulphates.—Sodium thiosulphate is the salt manufactured in largest quantity and it finds application for a variety of purposes, for example, as an "antichlor" for the removal of traces of chlorine from bleached linen, cotton, paper, etc., and also mixed with sodium carbonate for the absorption of chlorine fumes. For this latter purpose it was used in the earlier types of respirators during the Great War. On account of its ability to dissolve silver halides, sodium thiosulphate in aqueous solution is used as a "fixer" in photography, and also may be used for the removal of silver chloride from the accompanying mineral matter in the extraction of silver from its ores. The aurothiosulphates of organic bases, for example of ethylene diamine, have been suggested for medicinal use.

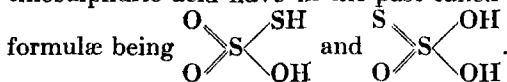
In chemical analysis, sodium thiosulphate is applicable in various directions. It is frequently of value for the precipitation of metals in the form of sulphides,² and occasionally provides a convenient method for the separation of two metals, *e.g.* copper from zinc; more especially, however, it finds use as a standard volumetric reagent for iodometric processes, but its use as a standard can even be extended to acidimetry and alkalimetry, the reaction



allowing a standard solution of sodium thiosulphate to be used for checking alkali solutions for volumetric analysis (see p. 205).

Fused hydrated sodium thiosulphate may be used as a cryoscopic solvent.³

Constitution.—The claims of two formulæ for the constitution of thiosulphuric acid have in the past called for serious consideration, the



The latter is of more recent date and the evidence in its favour is not very considerable. From the fact that sulphuryl chloride is not produced by the action of phosphorus pentachloride on sodium thio-

sulphate, the absence of the $\begin{array}{c} \text{O} \\ \parallel \\ \text{S} \\ \parallel \\ \text{O} \end{array} \diagdown$ grouping has been argued;⁴ the

reaction between an alkali thiosulphate and potassium cyanide with

¹ Nabl, *Ber.*, 1900, 33, 3554; *Monatsh.*, 1901, 22, 737; Willstätter, *Ber.*, 1903, 36, 1831; Abel, *Zeitsch. Elektrochem.*, 1911, 18, 705; 1913, 19, 480; *Monatsh.*, 1907, 28, 1239; 1913, 34, 177, 425, 821; Tarugi and Vitali, *Gazzetta*, 1909, 39, i., 418.

² Himly, *Annalen*, 1842, 43, 150; Vohl, *ibid.*, 1855, 96, 273; Westmoreland, *J. Soc. Chem. Ind.*, 1886, 5, 51; Zimmermann, *Zeitsch. anal. Chem.*, 1888, 27, 62.

³ Bontaric, Chauvenet and Nabot, *Compt. rend.*, 1924, 178, 571.

⁴ Buchanan, *Ber.*, 1870, 3, 485; Blomstrand, *ibid.*, p. 960.

formation of alkali sulphite and potassium thiocyanate ¹ has also been adduced as an argument in favour of the dihydroxy constitution, as also has the apparently analogous instability of thiosulphuric and sulphurous acids as compared with sulphuric acid.²

The fact that the ultimate products of the atmospheric oxidation of sodium thiosulphate are sulphur dioxide and sodium sulphate may be explained by assuming a primary decomposition into sulphite and sulphur (traces of the latter always being present in the salt), and subsequent oxidation of these.³

On the other hand, much stronger evidence is available in favour of the earlier formula,⁴ which accords well with the relationship between the acid and the polythionic acids.⁵ The formation of sodium thiosulphate by Spring's synthesis from sodium sulphide and sodium sulphite (p. 194) is definitely favourable to this constitution, as also especially is the fact that an alkali thiosulphate will react with only an equimolecular proportion of an organic (alkyl) halide,⁶ the product

most certainly having the constitution $\begin{array}{c} \text{O} \quad \text{SR} \\ \diagdown \quad \diagup \\ \text{S} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{OM} \end{array}$, where M represents

the alkali metal and R the newly introduced organic radical. For example, in sodium ethyl thiosulphate, the juxtaposition of the ethyl radical and the sulphur atom is clearly proved by the facts that acids cause the production of ethyl hydrogen sulphide, $\text{C}_2\text{H}_5\cdot\text{SH}$,⁶ whilst electrolytic reduction or the action of alkali yields ethyl disulphide⁷ and oxidation produces ethyl sulphonic acid, $\text{C}_2\text{H}_5\cdot\text{SO}_2\cdot\text{OH}$.⁶

In view of such evidence it appears impossible to avoid the conclusion that the two hydrogen atoms in thiosulphuric acid must be differently linked to the central atom, namely by a sulphur atom and

an oxygen atom, respectively. The formula $\begin{array}{c} \text{O} \quad \text{SH} \\ \diagdown \quad \diagup \\ \text{S} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{OH} \end{array}$ is also stated

to agree better with the strength of the acid, as shown by the relative inertness of the alkali salts towards acetic acid,⁸ and with the electrolytic conductivity of the salts.⁹

Indications have been obtained of isomeric salts ¹⁰ of the constitutions

$\begin{array}{c} \text{O} \quad \text{ONa} \\ \diagdown \quad \diagup \\ \text{S} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{SK} \end{array}$ and $\begin{array}{c} \text{O} \quad \text{OK} \\ \diagdown \quad \diagup \\ \text{S} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{SNa} \end{array}$, and if such a result could be placed

beyond doubt, convincing evidence of the correctness of this formula for the acid would be forthcoming; the result, however, needs careful re-examination.

¹ Gutmann, *Ber.*, 1905, 38, 1728, 3276; 1906, 36, 509; 1907, 40, 3614.

² Buchanan, *loc. cit.*; Blomstrand, *loc. cit.*

³ Picon, *Compt. rend.*, 1924, 178, 1548.

⁴ Odling, *Trans. Chem. Soc.*, 1869, 22, 180, 256; Schorlemmer, *ibid.*, p. 254; Williamson, *ibid.*, p. 259.

⁵ Mendeléeff, *Ber.*, 1870, 3, 870.

⁶ Bunte, *ibid.*, 1874, 7, 646.

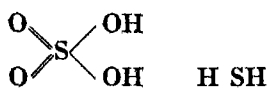
⁷ Price and Twiss, *Trans. Chem. Soc.*, 1907, 91, 2021; 1908, 93, 1395; 1909, 95, 1489; Twiss, *ibid.*, 1914, 105, 36, 1672. For further reactions of organic thiosulphates, see Heller, *J. prakt. Chem.*, 1924, [ii.], 108, 257; Footner and Smiles, *Trans. Chem. Soc.*, 1925, 127, 2887.

⁸ Matthieu-Plessy, *Compt. rend.*, 1885, 101, 59.

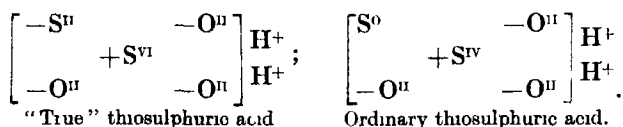
⁹ Walden, *Zeitsch. physikal. Chem.*, 1887, 1, 536.

¹⁰ Schwicker, *Ber.*, 1889, 22, 1733. See also Drechsel, *J. prakt. Chem.*, 1871, [ii.], 4, 20.

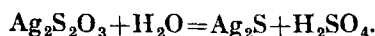
Such a constitution suggests that thiosulphuric acid is a mixed anhydride of sulphuric acid and hydrogen sulphide, thus :



and in aqueous solution one would expect decomposition to produce sulphuric acid and hydrogen sulphide rather than sulphurous acid and sulphur. Piccard and Thomas,¹ by allowing sulphur trioxide and hydrogen sulphide to react in carbon dioxide solution at the temperature of liquid air, obtained a product which they presumed to be the true mixed anhydride. This compound contained a sexavalent central sulphur atom, the added sulphur atom being in the place of a negative bivalent oxygen atom of sulphuric acid. Ordinary thiosulphuric acid was considered to be an electronic isomeride of this compound, with a quadrivalent central atom, the added sulphur atom being neutral. The differences are expressed in the following co-ordinative formulæ :²



Detection and Estimation.—The decomposition of thiosulphates by means of hydrochloric acid to yield sulphur dioxide with separation of sulphur serves as a primary identification test, the limit of sensitiveness being about 0.1 mg. S_2O_3 per c.c.³ The alkali thiosulphates produce with silver nitrate solution a white precipitate of thiosulphate which gradually turns yellow, then brown, and finally black, due to the formation of sulphide ; the change is accelerated by warming :⁴



This test is 100 times more sensitive than the acidification test.⁵

Precipitation with copper sulphate (see p. 200) also affords a test which is considerably more sensitive⁶ than the acidification test, and the result is not affected by the presence of polythionates.

Lead salts similarly yield a precipitate of thiosulphate, soluble in excess of alkali thiosulphate, which also blackens on warming, but the decomposition of the lead thiosulphate is less straightforward, a considerable quantity of sulphur being present in the greyish product.⁷ Barium chloride with a concentrated solution of an alkali thiosulphate forms a crystalline precipitate of sparingly soluble barium thiosulphate, of which one part dissolves in 480 of water at 18° C.⁸

A solution of a thiosulphate also exhibits certain striking colour

¹ Piccard and Thomas, *Helv. Chim. Acta*, 1923, 6, 1032

² Co-ordination formulæ have been suggested by others, see for example Feigl, *Ber.*, 1923, 56, [B], 2086.

³ Hackl, *Chem. Zest.*, 1923, 47, 174

⁴ Fogh, *Compt. rend.*, 1890, 110, 709, *Ann. Chim. Phys.*, 1890, [vi.], 21, 56.

⁵ Hackl, *loc. cit.*

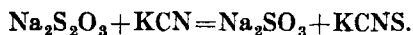
⁶ Riesenfeld and Grünthal, *Medd. K. Vet.-Akad. Nobel-Inst.*, 1925, 6, No. 9, 1.

⁷ Faktor, *Zetsch. anal. Chem.*, 1900, 39, 351; Norton, *Chem. News*, 1901, 89, 254; Perkins and King, *Trans. Chem. Soc.*, 1913, 103, 300.

⁸ Autenrieth and Windaus, *Zetsch. anal. Chem.*, 1898, 37, 290.

reactions.¹ With ferric chloride solution a transient violet colour is obtained. With sodium nitroprusside which has been exposed to the atmosphere until it has become brown, a blue coloration is produced,² whilst the thiosulphate solution, after reduction with sodium hydroxide and a little aluminium, gives with a fresh nitroprusside solution the violet colour characteristic of a sulphide.³ Very small quantities of a thiosulphate are sufficient to give a blue "ring test" when the solution is carefully poured on to a mixture of ammonium molybdate solution with concentrated sulphuric acid.⁴

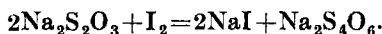
Other reactions readily available for the detection of a thiosulphate include reduction to hydrogen sulphide by most reducing agents, for instance by zinc and hydrochloric acid, oxidation to sulphuric acid or a sulphate, and formation of a thiocyanate on warming with an alkaline solution of a cyanide :⁵



When solutions of iodine and sodium azide are mixed, no reaction occurs, but in the presence of thiosulphate vigorous evolution of nitrogen occurs. The reaction is extremely sensitive,⁶ the thiosulphate being effective at a dilution of 1 in 6×10^6 , and is not brought about by elementary sulphur or by any other sulphur compound except sulphide (see p. 65) and thiocyanate.

The most trustworthy method for the gravimetric estimation of a pure thiosulphate is oxidation to sulphuric acid, for example by means of chlorine or bromine, or by the addition of an alkali salt of a halogen oxy-acid, and then precipitation with barium chloride.

Of volumetric processes, titration with iodine is the most commonly applied :⁷



An alternative principle for the volumetric determination is to apply an acidimetric process. The thiosulphate may be oxidised with hydrogen peroxide in the presence of a known quantity of an alkali in excess and the excess of alkali measured by titration with standard acid,⁸ or the oxidation may be effected with hydrogen peroxide alone and the resulting acidity directly titrated with a standard alkali :⁹



The acidimetric procedure may be applied, however, in quite a

¹ For a sensitive colour reaction in the presence of nitrous ions, see Falcioni, *Gazzetta*, 1922, 52, i., 179.

² Casolari, *Gazzetta*, 1910, 40, ii., 389.

³ De Koninck, *Zeitsch. anal. Chem.*, 1887, 26, 26.

⁴ Pozzi-Escot, *Bull. Soc. chim.*, 1913, [iv.], 13, 401.

⁵ Pechmann and Manok, *Ber.*, 1895, 28, 2377; Gutmann, *Zeitsch. anal. Chem.*, 1907, 46, 485.

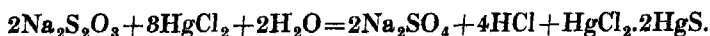
⁶ Feigl, *Zeitsch. anal. Chem.*, 1928, 74, 369.

⁷ For the use of the iodometric method in the analysis of mixtures containing sulphide, sulphite and thiosulphate, see Kurtenacker and others, *Zeitsch. anorg. Chem.*, 1924, 141, 297; 1927, 161, 201; and for mixtures of sulphide, polysulphide and thiosulphate, see Schulek, *Zeitsch. anal. Chem.*, 1925, 65, 352. For titration methods using potassium iodate, see Jamieson, *Amer. J. Sci.*, 1915, 39, 639; also Ivanoff, *J. Russ. Phys. Chem. Soc.*, 1914, 46, 419; Dimitrow, *Zeitsch. anorg. Chem.*, 1924, 136, 189.

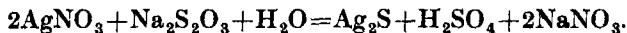
⁸ Eliasberg, *Ber.*, 1888, 19, 320.

⁹ Beason, *Chem. Zeit.*, 1913, 37, 920.

different manner; mercuric chloride reacts with thiosulphate solutions giving rise to a white precipitate of a "thiochloride," $\text{Hg}_3\text{S}_2\text{Cl}_2$ or $\text{HgCl}_2 \cdot 2\text{HgS}$, the equation being:



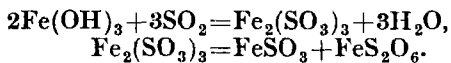
By titration of the resulting acid the original quantity of thiosulphate can be calculated. This method has the especial advantage of being applicable in the presence of sulphides, which give a similar precipitate, but do not produce acidity.¹ A similar process has been proposed using silver nitrate as precipitant:²



The Polythionic Acids.

The term "polythionic acids" covers a group of acids³ of the general formula $\text{H}_2\text{S}_x\text{O}_6$, where x may range from 2 to 6, the various members of the group being distinguished by the names dithionic acid, trithionic acid, etc.

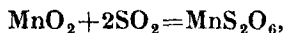
Dithionic Acid, $\text{H}_2\text{S}_2\text{O}_6$, is obtained only in aqueous solution. If sulphur dioxide is passed into an aqueous suspension of ferric hydroxide at 0°C ., a red solution of ferric sulphite is first produced, which then changes to a pale green solution of ferrous sulphite and ferrous dithionate:⁴



By the addition of barium hydroxide to the solution, a solution of barium dithionate can be obtained which, on treatment with the necessary quantity of sulphuric acid, yields a dilute solution of dithionic acid; this can be concentrated to some extent by evaporation at the ordinary temperature, but if the concentration is carried too far, decomposition ensues, with formation of sulphur dioxide and sulphuric acid. If so desired, the barium dithionate itself may be isolated by removing the excess of barium hydroxide with a current of carbon dioxide and then allowing the solution to evaporate until crystallisation occurs.

In the foregoing process it will be seen that the ferric hydroxide, in effect, acts as an oxidising agent. Other oxidising agents are also applicable, but the results are less satisfactory than with ferric hydroxide.

The process by which Gay-Lussac and Welter⁵ discovered dithionic acid was the oxidation of sulphurous acid with manganese dioxide; the reaction is frequently represented as



but in reality it is more complex and the dithionate is always accompanied by a preponderating quantity of sulphate. Although it is

¹ Sander, *Zeitsch. angew. Chem.*, 1915, 28, 9; 1916, 29, 11, 16; *Zeitsch. anal. Chem.*, 1916, 55, 340; *Chem. Zest.*, 1915, 39, 945; Feld, *Zeitsch. angew. Chem.*, 1911, 24, 1161.

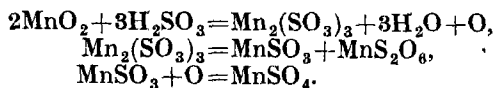
² Bodnár, *Zeitsch. anal. Chem.*, 1913, 53, 37.

³ Debus, *Trans. Chem. Soc.*, 1888, 53, 278.

⁴ Gélis, *Ann. Chim. Phys.*, 1862, [iii.], 65, 222; Seubert and Elten, *Zeitsch. anorg. Chem.*, 1893, 4, 86; Carpenter, *Proc. Chem. Soc.*, 1901, 17, 212; Antony, *Gazzetta*, 1902, 32, i., 514; Antony and Manasse, *ibid.*, 1899, 29, i., 483; Meyer, *Ber.*, 1902, 35, 3429.

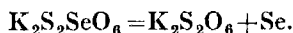
⁵ Gay-Lussac and Welter, *Ann. Chim. Phys.*, 1819, 10, 312.

possible that the dithionate and sulphate are produced by two independent concurrent reactions,¹ the dithionate reaction being favoured by a low temperature whilst rise in temperature favours the production of sulphate, the more probable course of the change is the primary formation of manganic sulphite, which subsequently decomposes, giving manganous sulphite and dithionate,² in a manner analogous to that described with ferric hydroxide :

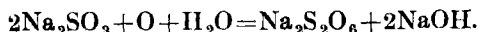


This view is favoured by the observation that not only does ferric hydroxide give a similar result, but manganese trihydroxide and cobalt trihydroxide also produce a small quantity of dithionate,³ whereas the peroxides, which generally are derived from metals of unvarying valency (see Vol. VII., Part I., of this Series, p. 54), oxidise sulphurous acid only to sulphuric acid or a sulphate. Lead dioxide⁴ reacts but very slightly with sulphurous acid, probably on account of the sparing solubility of the products, which coat the particles of dioxide and prevent further action. Chromates and dichromates⁵ in acid solution convert sulphurous acid to a small extent into dithionic acid, and again it will be noticed that the metal, in this case chromium, is of variable valency. Permanganates⁶ give a similar result with sulphurous acid, and even gradual atmospheric oxidation⁷ of the acid or ammonium hydrogen sulphite solution will give rise to some dithionic acid.

Alkali sulphites in boiling aqueous solution dissolve selenium with formation of a selenotrihionate, which subsequently decomposes giving the alkali dithionate :⁸



Contrary to earlier views, alkali dithionate is not obtainable by the action of iodine on the corresponding alkali hydrogen sulphite,⁹ sulphate being the sole product given. Conversion of sulphite into dithionate, however, can be effected by *electrolysis*,¹⁰ the results not being due to the coupling of discharged sulphite ions but to anodic oxidation of the sulphite, sulphate also being formed :



The electrodes should be of smooth platinum, and the yield is increased if the anode is heated for a short time immediately before use. Previous

¹ Spring and Bourgeois, *Bull. Soc. chim.*, 1886, [ii.], 46, 151.

² Meyer, *Ber.*, 1901, 34, 3606; 1902, 35, 3429.

³ Carpenter, *loc. cit.*

⁴ Rammelsberg, *Ann. Phys. Chem.*, 1846, [ii.], 67, 504.

⁵ Berthier, *Ann. Chim. Phys.*, 1843, [iii.], 7, 77; Bassett, *Proc. Chem. Soc.*, 1903, 19, 54.

⁶ Péan de St. Gilles, *Ann. Chim. Phys.*, 1859, [iii.], 55, 374; Buignet, *J. Pharm.*, 1859, [iii.], 36, 113; Dymond and Hughes, *Proc. Chem. Soc.*, 1897, 71, 314.

⁷ Jacquelin, *Ann. Chim. Phys.*, 1847, [iii.], 21, 110; Rochleder, *Sitzungsber. K. Akad. Wiss. Wien*, 1856, 22, 280.

⁸ Rathke and Zschiesche, *J. prakt. Chem.*, 1864, 92, 141; Rathke, *ibid.*, 1866, 97, 56.

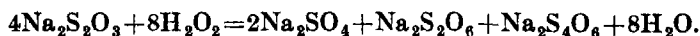
⁹ Sokolow and Marchlewski, *Ber.*, 1881, 14, 2058; Spring and Bourgeois, *Bull. Soc. chim.*, 1886, [ii.], 46, 151; 1891, [iii.], 6, 920; Otto, *Arch. Pharm.*, 1892, 239, 1.

¹⁰ Forster and Friessner, *Ber.*, 1902, 35, 2515; Friessner, *Zeitsch. Elektrochem.*, 1904, 10, 265; Essin, *ibid.*, 1928, 34, 78.

anode polarisation is also advantageous. Addition of ammonium fluoride, 0.1 per cent. maximal, increases the yield when the anode has not been preheated, but otherwise has an adverse effect. Under favourable conditions a yield of 45 per cent. of dithionic acid may be obtained, the maximum possible from theoretical considerations being about 50 per cent.

When silver sulphite or a mixture of sodium sulphite and silver nitrate is heated in boiling aqueous solution, decomposition occurs with formation of silver dithionate.¹

Thiosulphates, e.g. sodium thiosulphate, are oxidisable to polythionates by the addition of the requisite quantity of hydrogen peroxide. If the reaction mixture is allowed to become alkaline, dithionate, tetrathionate and sulphate are produced : ²



Oxidation of thiosulphate to dithionate can also be effected in dilute acetic acid solution with potassium permanganate ; ³ in alkaline solution, sulphate is the only product.

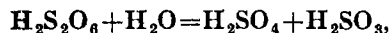
The acid is known only in aqueous solution and in the form of its salts, the *dithionates* or *hyposulphates*, the latter name now being infrequently used.

The aqueous solution is odourless, but possesses an acid taste ; its electrical conductivity shows that dithionic acid is to be classed amongst the strong acids.⁴ The heat of formation ⁵ of aqueous dithionic acid relative to its elements and the solvent is represented by the equation :



The molecular weight and basicity of the acid were at one time in question, the fact that no acid salts are formed giving the incorrect impression that the acid was monobasic.⁶ By Ostwald's method for the determination of the basicity of an acid from the increase in the molecular conductivity of an aqueous solution of the sodium salt on dilution,⁷ and by measurement of the molecular weights of the salts in aqueous solution,⁸ it was subsequently demonstrated that the acid is dibasic and of the double molecular formula $\text{H}_2\text{S}_2\text{O}_6$.

In aqueous solution at the ordinary temperature, the concentration of the acid cannot be raised beyond that corresponding with a specific gravity of 1.35, on account of decomposition according to the equation



which occurs at any concentration on heating.⁹ In dilute solutions

¹ Baubigny, *Compt. rend.*, 1910, 150, 466, 973.

² Nabl, *Monatsh.*, 1901, 22, 737.

³ Péan de St. Gilles, *loc. cit.* ; Fordos and Géhs, *J. Pharm.*, 1859, [iii.], 36, 122 ; Höng and Zatzek, *Ber.*, 1883, 16, 2661 ; Luckow, *Zeitsch. anal. Chem.*, 1893, 32, 53.

⁴ Ostwald, *J. prakt. Chem.*, 1885, [ii.], 32, 315, Hertlein, *Zeitsch. physikal. Chem.*, 1896, 19, 300.

⁵ Thomsen, *Ber.*, 1872, 5, 1016 ; 1873, 6, 1535, Berthelot, *Compt. rend.*, 1889, 108, 777.

⁶ Kolbe, *J. prakt. Chem.*, 1879, [ii.], 19, 485. See also Trey, *ibid.*, 1886, [ii.], 34, 353.

⁷ Ostwald, *Zeitsch. physikal. Chem.*, 1887, 1, 106.

⁸ Meyer, *Ber.*, 1901, 34, 3610.

⁹ Gay-Lussac and Welter, *Ann. Chim. Phys.*, 1819, 10, 312 ; Yost and Pomeroy, *J. Amer. Chem. Soc.*, 1927, 49, 703.

(3 to 4 per cent.) the decomposition proceeds to the extent of 3 per cent. in 945 hours at 25° C., and 20 per cent. in 245 hours at 47° C.¹

Dithionic acid solutions are remarkably resistant to oxidation; the cold solutions withstand the attack of hypochlorite, hypobromite and permanganic acid, although on boiling, these reagents become reduced by the sulphur dioxide liberated in the decomposition of the dithionic acid; sodium peroxide effects a partial oxidation in the cold.²

Reduction by sodium amalgam or by zinc and an acid produces sulphurous acid :³



The Dithionates or Hyposulphates.—These salts, like the nitrates, are all soluble in water; only normal salts are known.⁴ They may be obtained by neutralising dithionic acid solution with the hydroxide of the base, and also by double decomposition between barium dithionate solution and the sulphate of the base, or between manganese dithionate solution and the hydroxide of the base; ⁵ also by methods on pp. 206–8.

Sodium ethyl thiosulphate, $\text{SO}_2 \begin{matrix} \text{ONa} \\ \text{SC}_2\text{H}_5 \end{matrix}$, decomposes slowly at 100° C. with the formation of ethyl disulphide and sodium dithionate.⁶

SOLUBILITY OF DITHIONATES IN WATER AT 20° C.⁷

Salt.	Grams of Salt in 100 grams Solution
$\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$	13.39
$\text{K}_2\text{S}_2\text{O}_6$	6.23
$2(\text{NH}_4)_2\text{S}_2\text{O}_6 \cdot \text{H}_2\text{O}$	62.43
$\text{MgS}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$	33.91
$\text{CaS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$	20.25
$\text{SrS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$	10.80
$\text{BaS}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$	15.75
$\text{CuS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$	44.91

Of the dithionates, those of the alkali and alkaline earth metals are the most stable and may be heated in aqueous solution up to 100° C. without decomposition. When heated alone, the dithionates decompose readily with formation of sulphate and sulphur dioxide; some of them indeed are so unstable that they are not obtainable in a pure condition.

Mineral acids decompose dithionate solutions only on boiling, sulphate and sulphur dioxide then being produced; for this reason permanganate is decolorised only by hot acid solutions.⁸ Iodine solution is slowly

¹ de Baat, *Rec. Trav. chim.*, 1926, 45, 237.

² Longi and Bonavia, *Gazzetta*, 1898, 28, 1, 325.

³ Spring and Bourgeois, *Bull. Soc. chim.*, 1891, [iii], 6, 920, Otto, *Annalen*, 1868, 147, 187.

⁴ Muller, *Bull. Soc. chim.*, 1909, [iv.], 5, 1119, 1911, [iv.], 9, 183.

⁵ Hertlein, *Zeitsch. physikal. Chem.*, 1896, 19, 289.

⁶ Bunte, *Ber.*, 1874, 7, 647.

⁷ de Baat, *loc. cit.*

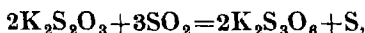
⁸ Carpenter, *Proc. Chem. Soc.*, 1901, 17, 212.

decolorised, due to the gradual formation of sulphurous acid, the final product being an acid sulphate.¹

In the presence of such reagents as bromate, iodate or dichromate, the rate of oxidation is independent of the nature or concentration of the oxidising agent, but is the same as the rate of decomposition to sulphate and sulphite, so that it is evident that hydrolysis is the first stage in the oxidation.²

For the constitution and estimation of dithionic acid and its salts, see later (pp. 221-4).

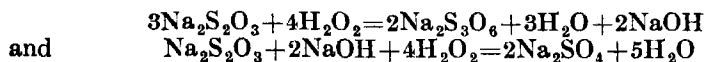
Trithionic Acid, $H_2S_3O_6$.—*Formation.*—(1) *From Thiosulphates:* Potassium thiosulphate in concentrated aqueous solution reacts with sulphur dioxide forming potassium trithionate; ³ the reaction is sometimes represented as



but this does not quantitatively represent the change, some tetrathionate and pentathionate also being produced, whilst the quantity of sulphur liberated is correspondingly less.⁴ The trithionate crystallises from the solution, and the free acid is obtained in the solution by treatment with hydrofluosilicic acid (see p. 211).

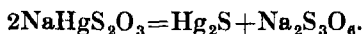
A similar formation of trithionate can be effected by recrystallising a mixture of potassium thiosulphate and potassium hydrogen sulphite in aqueous solution.⁵ It is probable that the method by which potassium trithionate was first prepared depended on the same reaction.⁶ Potassium hydrogen sulphite solution was warmed with sulphur for several days, with the result that sulphate, thiosulphate and trithionate were obtained, the formation of the last-named in all probability occurring by way of the thiosulphate.

By the gradual addition of hydrogen peroxide to an ice-cold aqueous solution of sodium thiosulphate, it is possible to convert the latter into trithionate, the changes



occurring simultaneously.⁷

Certain double salts of thiosulphuric acid when heated with water undergo decomposition with production of trithionate;⁸ thus the sodium-mercurous salt decomposes according to the equation:



At one time it was believed that trithionate could be synthetically produced by the action of iodine on an aqueous mixture of sodium

¹ Heeren, *Ann. Phys. Chem.*, 1826, [u.], 7, 55, Rammelsberg, *ibid.*, 1843, [u.], 59, 472; 1866, [u.], 128, 332; Kraut, *Annalen*, 1861, 118, 95; 1889, 250, 255; Fock, *Zeitsch. Kryst. Min.*, 1882, 6, 161; 1888, 14, 340; Fock and Kluss, *Ber.*, 1890, 23, 3001.

² Yost and Pomeroy, *loc. cit.*

³ Plessy, *J. prakt. Chem.*, 1844, 33, 348.

⁴ Debus, *Annalen*, 1888, 244, 170; Hertlein, *Zeitsch. physikal. Chem.*, 1896, 19, 291; Villiers, *Compt. rend.*, 1889, 108, 42; Baker, *Chem. News*, 1877, 36, 203.

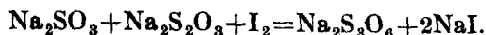
⁵ Rathke, *J. prakt. Chem.*, 1865, 95, 1.

⁶ Langlois, *Compt. rend.*, 1840, 10, 461; *Annalen*, 1841, 40, 102; *Compt. rend.*, 1866, 62, 842. See also Pierion, *Bull. Soc. chim.*, 1899, [u.], 21, 477, for another method of forming trithionic acid, probably depending on the interaction of sulphur dioxide and thiosulphate.

⁷ Willstätter, *Ber.*, 1903, 36, 1831; Tarugi and Vitali, *Gazzetta*, 1909, 39, 1, 418.

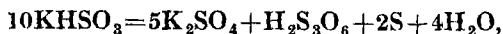
⁸ Spring, *Ber.*, 1874, 7, 1159.

sulphite and thiosulphate,¹ the reaction being assumed to accord with the equation:



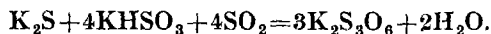
Subsequent investigation indicated that this view of the reaction was erroneous, and that any trithionate obtained was actually due to a secondary reaction between tetrathionate and sulphite.²

(2) *From Sulphites*: Potassium hydrogen sulphite, when kept in aqueous solution for a long time with exclusion of air, undergoes spontaneous change with formation of sulphate and trithionate.³ The change, which is commonly represented as

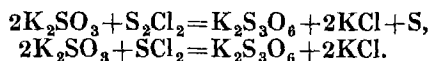


is possibly connected with the decomposition of sulphites into sulphate and sulphur (p. 132).

Trithionate is also produced when sulphur dioxide is passed into a mixture of solutions of potassium sulphide and potassium hydrogen sulphite: ⁴



Sulphur chloride or dichloride can convert potassium sulphite into trithionate,⁵ the equations being



(3) Trithionic acid is found together with sulphuric, sulphurous and thiosulphuric acids in the reaction product from the decomposition of nitrogen sulphide, N_4S_4 , with water.⁶

(4) In the oxidation of alkali sulphides or polysulphides by potassium permanganate solution at the ordinary temperature, trithionic acid has been found amongst the reaction products, in addition to sulphuric acid and sulphur.⁷

(5) The spontaneous degradation of the higher polythionates gives rise to trithionate (see p. 219).

Properties.—Trithionic acid is the least stable of the polythionic acids. The aqueous solution of the free acid, which is generally obtained from a cold concentrated solution of the potassium salt by the addition of a suitable acid, such as hydrofluosilicic or perchloric acid, which will remove the metal as a sparingly soluble salt, slowly decomposes, even at the ordinary temperature, with formation of sulphur, sulphur dioxide and sulphuric acid:



The decomposition is really due to hydrolysis, the primary products being sulphuric and thiosulphuric acids, the formation of the former causing the decomposition of the latter,⁸ the presence of which is consequently difficult to detect (see p. 213).

¹ Spring, *loc. cit.*; *Chem. News*, 1892, 65, 247.

² Colefax, *Chem. News*, 1892, 65, 47; 66, 292; *Trans. Chem. Soc.*, 1892, 61, 181, 1083.

³ Saint-Pierre, *Compt. rend.*, 1866, 62, 632.

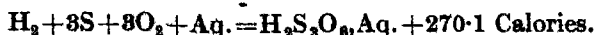
⁴ Chancel and Diacon, *ibid.*, 1863, 56, 710.

⁵ Spring, *Ber.*, 1873, 6, 1108. See also Debus, *Annalen*, 1888, 244, 172.

⁶ Ruff and Geisel, *Ber.*, 1904, 33, 1573. ⁷ Honig and Zatzek, *ibid.*, 1883, 16, 2661.

⁸ Foerster, *Zeitsch. anorg. Chem.*, 1925, 144, 337.

The pure acid has not been isolated, but the moderately concentrated solution is an odourless, clear, slightly viscous liquid, which is not very strongly acidic, although it possesses an acid taste. The heat of formation¹ of the acid from its elements is given by the equation:



Oxidising acids such as nitric, chloric and iodic acids induce rapid decomposition of trithionic acid with formation of sulphur and sulphuric acid;² the presence of other acids, for example hydrochloric, perchloric or dilute sulphuric acid, also hydrogen sulphide, is without any harmful effect.³ Addition of sulphurous acid causes the gradual formation of a mixture of all the polythionic acids.

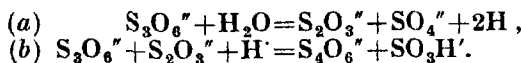
Copper nitrate and mercuric nitrate when heated with the aqueous solution give a black precipitate of the corresponding sulphide; mercuric chloride in excess causes the precipitation of the white substance $2\text{HgS} \cdot \text{HgCl}_2$ (see p. 206); silver nitrate produces a white precipitate which gradually becomes black due to the formation of sulphide.⁴

The Trithionates.—These salts are of the general type $\text{X}_2\text{S}_3\text{O}_6$, where X represents the equivalent weight of a metal; the alkali salts are the best known.⁵

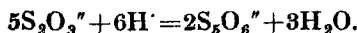
When heated alone the salts decompose with liberation of sulphur and sulphur dioxide:⁶



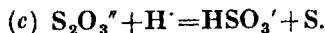
In aqueous solution alkali trithionates gradually undergo decomposition with formation of sulphate, hydrogen sulphite and tetrathionate. The course of the main reaction may be expressed ionically as follows:⁷



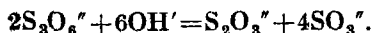
A trace of pentathionate is also found in the solution after the lapse of several days, probably formed according to



The decomposition is accelerated by the presence of acid, and sulphur is deposited:



In the presence of alkali⁸ decomposition is fairly rapid, sulphite and thiosulphate being the chief products:



¹ Thomsen, *Ber.*, 1872, 5, 1019; Berthelot, *Compt. rend.*, 1889, 108, 775. See Abegg, *Handbuch der Anorganischen Chemie*, vol. iv, 1, p. 556 (Leipzig, 1927).

² Keasler, *Ann. Phys. Chem.*, 1848, [n.], 74, 250; Langlois, *Compt. rend.*, 1840, 10, 461.

³ Fordos and Gélis, *Ann. Chim. Phys.*, 1850, [m.], 28, 451; Spring, *Ber.*, 1874, 7, 1159.

⁴ Spring, *loc. cit.* See also Willstätter, *Ber.*, 1903, 36, 1831.

⁵ Mackenzie and Marshall, *Trans. Chem. Soc.*, 1908, 93, 1726; Marshall, *J. Soc. Chem. Ind.*, 1897, 16, 396.

⁶ Langlois, *loc. cit.*

⁷ Kurténacker and Kaufmann, *Zeitsch. anorg. Chem.*, 1925, 148, 43, 225, 256, 369. See also Debus, *loc. cit.*; Pelouze, *Ann. Chim. Phys.*, 1840, 79, 85.

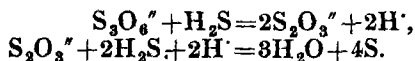
⁸ Fordos and Gélis, *Ann. Chim. Phys.*, 1850, [m.], 28, 451; *J. prakt. Chem.*, 1850, 50, 86; Muck, *Ber.*, 1871, 4, 446; Spring, *loc. cit.*; Berthelot, *Compt. rend.*, 1889, 108, 927; Foerster and Horning, *Zeitsch. anorg. Chem.*, 1922, 125, 86; Kurténacker and Kaufmann, *loc. cit.*

Thiosulphate is the sole product on treatment with an alkali sulphide : ¹



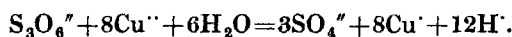
The decomposition of trithionates in aqueous solution is only slightly influenced by the addition of sulphites or thiosulphates, although the latter catalytically accelerate the decomposition of tetra- or pentathionates under similar conditions.²

In the presence of hydrogen sulphide the reaction is extremely slow, and is retarded by the presence of acid :



On adding potassium trithionate to a cold solution of copper acetate and keeping for several days in the dark, transparent yellow monoclinic prisms separate. These have the composition $K_2S_2O_3 \cdot Cu_2S_2O_3 \cdot 2H_2O$, i.e. potassium cuprous thiosulphate. They are unstable in air or on boiling with water, cupric sulphide being formed.³ This reaction demonstrates the formation of thiosulphate during the hydrolysis of trithionate solutions (cf. p. 211).

The trithionates may be quantitatively precipitated by boiling for one hour with a mixture of copper sulphate and barium chloride solutions containing free hydrochloric acid : ⁴



Tetrathionates and thiosulphates interfere, but not penta- or hexathionates.

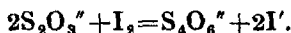
The salts derived from metals other than the alkali metals are relatively little known ; all are stated to be easily soluble in water with the exception of the mercurous, mercuric and silver salts, which are sparingly soluble. In describing the properties of the acid mention has already been made of the precipitation reactions of the salts with silver nitrate and other salts, and of the behaviour of the salts towards the alkali hydroxides and sulphides.

For the *constitution* and *estimation* of the acid and its salts, see p. 221.

Tetrathionic Acid, $H_2S_4O_6$.—*Formation.*—(1) *From Thiosulphates:* As is well known, sodium tetrathionate is produced by the interaction of sodium thiosulphate and iodine :



This reaction, discovered by Fordos and Gélis⁵ in 1842, is a general one and applicable to all thiosulphates ; it is ionic in character⁶ and therefore proceeds rapidly :



By using lead or barium thiosulphate a solution of the corresponding tetrathionate can be obtained from which an aqueous solution of the

¹ Chancel and Diacon, *J. prakt. Chem.*, 1863, 90, 55.

² Kurtenacher and Kaufmann, *loc. cit.*

³ Hornig, *Zeitsch. anorg. Chem.*, 1928, 176, 423.

⁴ Riesenfeld and Sydow, *ibid.*, 1928, 175, 74.

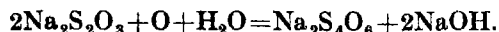
⁵ Fordos and Gélis, *Compt. rend.*, 1842, 15, 920 ; *Ann. Chim. Phys.*, 1843, [iii.], 8, 349 ; Sander, *Zeitsch. angew. Chem.*, 1915, 28, 273 ; Portillo, *Anal. Fis. Quim.*, 1929, 27, 236, 351.

⁶ Hertlein, *Zeitsch. physikal. Chem.*, 1896, 19, 289.

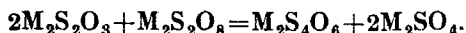
free acid may be prepared by treatment with the calculated quantity of dilute sulphuric acid. Lead thiosulphate gives better results than the barium salt, but it is not advisable to use hydrogen sulphide for the removal of the lead on account of the possible interaction of the hydrogen sulphide or the lead sulphide with the tetrathionic acid. On adding the requisite quantity of tartaric acid to a solution of potassium tetrathionate,¹ the potassium is gradually deposited as the hydrogen tartrate and a pure solution of tetrathionic acid obtained after one or two days.

Chlorine, bromine, hypochlorous acid and hypobromous acid also convert thiosulphate into tetrathionate, but their activity is so great that the reaction tends to proceed still further, with formation of sulphate.²

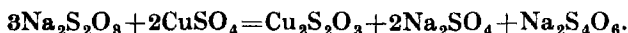
Many other oxidising agents can effect the same change in a thiosulphate, for example permanganates,³ chlorates,⁴ selenium dioxide,⁵ barium peroxide,⁶ hydrogen peroxide⁷ and lead dioxide,⁶ in the presence of sufficient sulphuric acid to neutralise the alkali as it is produced :



Perdisulphates likewise oxidise thiosulphates to tetrathionates, but do not need the presence of additional acid :⁸



Ferric salts and cupric salts are also able to convert thiosulphate into tetrathionate⁹ (see also p. 201). The reaction with copper sulphate is as follows :



A convenient method of preparing the potassium salt is to use this reaction, filter off the copper salt and to the concentrated filtrate add potassium acetate, when the tetrathionate separates ; this, after removal, should be washed with alcohol.¹⁰

The observation that in the electrolysis of ammonium thiosulphate solution tetrathionic acid is formed at the anode also belongs to this class, because the process is not one of the coupling of discharged anions, but an anodic oxidation of the thiosulphate.¹¹

Sulphur dioxide when passed through a solution of a thiosulphate gives rise not only to tetrathionate but also to trithionate and pentathionate.¹² Under suitable conditions, however, with a high concentration of sulphur dioxide, the tetrathionate separates. The reaction is accelerated by traces of potassium arsenite.¹³

¹ Debus, *Annalen*, 1888, 244, 148.

² Hertlein, *loc. cit.* ; Lunge, *Ber.*, 1879, 12, 404 ; Fordos and Gélis, *loc. cit.*

³ Spring and Levy, *Bull. Acad. roy. Belg.*, 1876, 42, 103.

⁴ Sonstadt, *Chem. News*, 1872, 26, 98.

⁵ Norris and Fay, *Amer. Chem. J.*, 1896, 18, 703 ; 1901, 23, 119.

⁶ Chancel and Diacon, *Compt. rend.*, 1863, 56, 710.

⁷ Nabl, *Ber.*, 1900, 33, 3554.

⁸ Marshall, *J. Soc. Chem. Ind.*, 1897, 16, 396 ; Marshall and Mackenzie, *Trans. Chem. Soc.*, 1908, 93, 1726.

⁹ Vortmann, *Ber.*, 1889, 22, 2307.

¹⁰ Raschig, *Schwefel- und Stickstoff-Studien*, 1924, p. 273 ; *Chem. Zeit.*, 1924, ii., 1065.

¹¹ Pierron, *Bull. Soc. chim.*, 1899, 21, 477 ; Thatcher, *Zeitsch. physikal. Chem.*, 1904, 47, 691.

¹² Debus, *Annalen*, 1888, 244, 169 ; Villiers, *Ber.*, 1889, 22, 222.

¹³ Terres and Overdick, *Gas- u. Wasserfach*, 1928, 71, 49, 81, 106, 130.

In the interaction of sulphur monochloride with potassium thio-sulphate, tetrathionate is obtained as the highest polythionate product.¹

(2) Tetrathionic acid is present in the mixture obtained by the action of sulphur dioxide on hydrogen sulphide in aqueous solution (see "Wackenroder's solution," p. 220).

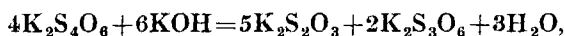
(3) Pentathionic acid solution when treated with lead dioxide² or when merely allowed to undergo spontaneous decomposition, yields tetrathionic acid.

Properties.—The free acid is known only in the form of its aqueous solution, which is without colour or odour.

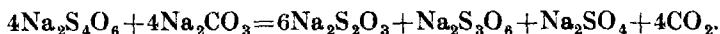
From the strongly acid taste, the heat of neutralisation with dilute sodium hydroxide³ and the electrical conductivity of the solution,⁴ it appears that tetrathionic acid is a fairly strong acid,⁵ comparable with dithionic acid in this respect. The heat of formation⁶ is given by the equation:



It is the most stable of the polythionic acids,⁷ and a dilute aqueous solution can be heated to boiling without decomposition, although the concentrated solution undergoes decomposition giving sulphurous and sulphuric acids together with sulphur.⁸ Mineral acids, excluding those of decided oxidising or reducing character, do not induce decomposition of the cold solutions. Alkalis, however, cause the formation of a mixture of thiosulphate and trithionate:



whilst in hot solution some sulphide may also be produced.⁹ With sodium carbonate the reaction is¹⁰



Sulphur dioxide abstracts sulphur from aqueous tetrathionic acid giving trithionic acid, the sulphur remaining in the solution and converting part of the tetrathionic acid into pentathionic acid, so that the final solution contains all three acids.¹¹

Hydrogen sulphide in excess causes gradual decomposition, sulphur

¹ Spring, *Bull. Acad. roy. Belg.*, 1881, [m.], 1, No. 2.

² Chancel and Diacon, *loc. cit.*

³ Thomsen, *Ber.*, 1872, 5, 1017.

⁴ Ostwald, *J. prakt. Chem.*, 1885, 32, 316; Hertlein, *Zeitsch. physikal. Chem.*, 1896, 19, 300.

⁵ Kolthoff (*Rec. Trav. chim.*, 1924, 23, 216) considers this acid to be one of the strongest dibasic acids.

⁶ Thomsen, *loc. cit.*; Berthelot, *Compt. rend.*, 1889, 108, 775.

⁷ Josephy, *Zeitsch. anorg. Chem.*, 1924, 135, 21. Cf. Riesenfeld and Feld (*ibid.*, 1921, 119, 225), who consider it the least stable. See further, Foerster, *ibid.*, 1924, 139, 226; Riesenfeld, *ibid.*, 1924, 141, 109; Kurtenacker and Kaufmann, *ibid.*, 1925, 148, 43.

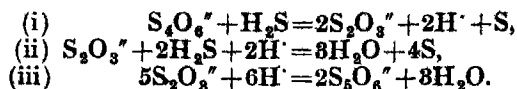
⁸ Fordos and Gélis, *loc. cit.*

⁹ Kurtenacker and Kaufmann, *Zeitsch. anorg. Chem.*, 1925, 148, 369. See also Fordos and Gélis, *loc. cit.*; Takamatsu and Smith, *Trans. Chem. Soc.*, 1880, 37, 592; 1882, 41, 162; Lewes, *ibid.*, 1882, 41, 300; Thatcher, *Zeitsch. physikal. Chem.*, 1904, 47, 691; Gutmann, *Ber.*, 1905, 38, 1728; 1907, 40, 3614; 1908, 41, 300; Chapin, *J. Amer. Chem. Soc.*, 1916, 38, 825.

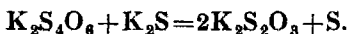
¹⁰ Raschig, *loc. cit.*

¹¹ Debus, *Annalen*, 1884, 244, 154.

and pentathionic acid being the chief products. In neutral solution the reaction is more rapid and appears to take the following course :¹

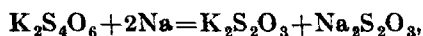


With the free acid only reactions (i) and (iii) occur. The decomposition takes place more readily than in the case of trithionic acid. Alkali sulphides in boiling solution convert tetrathionate into thiosulphate, with liberation of sulphur :²



Freshly precipitated lead sulphide also induces the decomposition of tetrathionic acid.

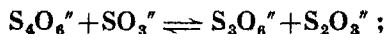
Vigorous oxidising agents, such as chlorine and bromine, convert tetrathionic acid into sulphuric acid, whilst reducing agents, for example hydrogen,³ especially in contact with platinum, and sodium or potassium amalgam,⁴ act on the tetrathionates with formation of thiosulphates,



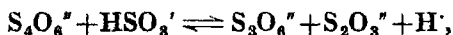
the reaction being capable of proceeding further, with the production of some sulphide.

The Tetrathionates.—These are generally soluble in water and can be caused to crystallise from solution by the addition of alcohol. When heated in solution the alkali salts decompose into trithionate and sulphur; further change may also give rise to pentathionate, sulphate and sulphite. Aqueous solutions are less stable in the presence of thiosulphate.⁵ The salts of the other metals, for example barium or copper, are much less stable, the former readily forming thiosulphate⁶ and the latter sulphide.²

The tetrathionates are converted by nascent sulphur into pentathionates, whilst by potassium sulphite solution they are reduced to trithionate.⁷ The latter reaction explains the erroneous assumption that trithionate could be directly produced by the action of iodine on an aqueous mixture of potassium thiosulphate and sulphite⁸ (see p. 210). With equivalent quantities of tetrathionate and sulphite, the reaction leads to the equilibrium⁹



but very slight excess of sulphite serves to send the reaction completely to the right. With a bisulphite the following equilibrium is slowly set up :



¹ Kurtenacker and Kaufmann, *Zeitsch. anorg. Chem.*, 1925, 148, 256.

² Chancel and Diacon, *loc. cit.*; Smith and Takamatsu, *Trans. Chem. Soc.*, 1882, 41, 162.

³ Thatcher, *Zeitsch. physikal. Chem.*, 1904, 47, 691.

⁴ Spring, *Ber.*, 1874, 7, 1161; Lewes, *Trans. Chem. Soc.*, 1882, 41, 300.

⁵ Sander, *Zeitsch. angew. Chem.*, 1915, 28, 273. See also Calzolari, *Atti R. Accad. Lincei*, 1915, [v.], 24, i., 921.

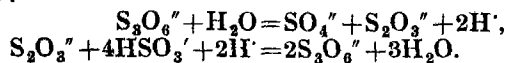
⁶ Hertlein, *Zeitsch. physikal. Chem.*, 1896, 19, 300.

⁷ Spring, *Chem. News*, 1892, 65, 247; Colefax, *Trans. Chem. Soc.*, 1908, 93, 798; Kurtenacker and Kaufmann, *Zeitsch. anorg. Chem.*, 1925, 148, 225.

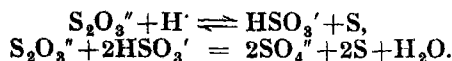
⁸ Spring, *loc. cit.*

⁹ Foerster and Centner, *Zeitsch. anorg. Chem.*, 1926, 157, 45.

but this is soon disturbed by decomposition and reformation of the trithionate, thus :



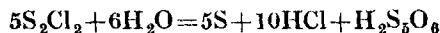
Thus the H' -ion concentration increases and sulphur separates :



Addition of excess of mercuric chloride to a solution of a tetrathionate causes precipitation of the compound $\text{Hg}_3\text{S}_4\text{Cl}_2$ (see pp. 212, 223).

Pentathionic Acid, $\text{H}_2\text{S}_5\text{O}_6$.—This is present in "Wackenroder's solution" ¹ (p. 220), and can be separated by removing the sulphuric acid by treatment with a little barium carbonate, the remaining acid liquid after filtration being capable of concentration to a specific gravity of 1.3 by evaporation on a water-bath and to 1.6 by evaporation in a vacuum at the ordinary temperature.² The solution contains also tetrathionic acid, which may be eliminated by the method described on p. 219.

The decomposition of sulphur monochloride by water gives rise to a complex mixture of substances including sulphur and pentathionic acid. The equation



originally suggested ³ to represent the change does not represent all the facts, because trithionic and tetrathionic acids are also present, and it is probable that the result may depend on a primary formation of thiosulphuric acid by the combination of nascent sulphur with sulphurous acid.⁴

When thiosulphates are decomposed by acids a small quantity of pentathionic acid, together with tetrathionic acid, is produced, in addition to sulphur and sulphur dioxide.⁵ Lead thiosulphate appears especially to be well adapted to this reaction and gives some pentathionic acid on treatment with iodine and hydriodic acid ⁶ or with hydrogen sulphide.⁷

The acid may be prepared free from tri- and tetra-thionic acids ⁸ by treating a cold aqueous solution of sodium thiosulphate containing sodium arsenite with hydrochloric acid. On concentrating the liquid at 35° C. sodium pentathionate gradually separates. After filtering, a solution is obtained containing about 60 per cent. of pentathionic acid together with a further 12 per cent. of the sodium salt.

By allowing the reaction to proceed at -10° to -15° C. mixed crystals of penta- and hexa-thionates may be obtained.⁹

¹ Wackenroder, *Annalen*, 1846, 60, 189.

² Kessler, *Ann. Phys. Chem.*, 1848, [ii.], 74, 249; *Ber.*, 1880, 13, 424.

³ Plessy, *Compt. rend.*, 1845, 21, 473; *Ann. Chim. Phys.*, 1847, [iii.], 20, 162; Fordos and Gélis, *ibid.*, 1848, [iii.], 22, 66; 1850, [iii.], 28, 451.

⁴ Debus, *Trans. Chem. Soc.*, 1888, 53, 278; *Annalen*, 1888, 244, 172.

⁵ Chancel and Diacon, *Compt. rend.*, 1863, 56, 710; Vortmann, *Ber.*, 1889, 22, 2307; Salzer, *Ber.*, 1886, 19, 1696.

⁶ Takamatsu and Smith, *Trans. Chem. Soc.*, 1880, 37, 592. See also Spring, *Annalen*, 1880, 201, 307.

⁷ Persoz, *Compt. rend.*, 1840, 10, 575; *Ann. Phys. Chem.*, 1865, [ii.], 124, 257.

⁸ Raschig, *Schwefel- und Stickstoff-Studien*, 1924, p. 273.

⁹ Kurtenacker and Czernotzky, *Zeitsch. anorg. Chem.*, 1928, 174, 179.

Pentathionic acid is formed by the action of sulphur dioxide on a suspension of sulphur in water : ¹



This reaction probably explains the formation of the acid by decomposition of thiosulphates by acids as already described.

Traces of pentathionic acid are also stated to be found in the condensed liquid from the interaction of steam and sulphur vapour at a red heat,² and in a mixture of sulphur and water after exposure to atmospheric oxidation.³ In the former case the pentathionic acid probably results after the high temperature reaction by the interaction of sulphur dioxide and hydrogen sulphide in the condensate.

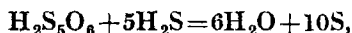
Properties.—Like the lower members of the series of thionic acids, free pentathionic acid is known only in aqueous solution; a solution of the pure acid is obtained by treating an aqueous solution of the potassium salt with the requisite quantity of tartaric acid for the removal of the potassium in the form of hydrogen tartrate. The solution is denser than water; ⁴ it cannot be concentrated beyond a limit of 50 to 60 per cent. acid without decomposition.

The heat of formation of the acid is given by the equation:



The solution is a colourless, odourless liquid of strongly acid taste and conducts the electric current.⁶ When cold it is comparatively stable,⁷ and may be kept practically unchanged for two or three months, but there is a tendency, especially with more concentrated solutions, to gradual decomposition with formation of tetrathionic acid, trithionic acid and sulphur; on boiling, the solution gives hydrogen sulphide and sulphur, together with sulphurous and sulphuric acids, the relative proportions varying with the concentration.

Hydrogen sulphide slowly decomposes aqueous pentathionic acid, the final state being represented by the equation



whilst excess of sulphurous acid causes a partial degradation into tetrathionic acid and trithionic acid.⁸

Oxidising agents such as chlorine water, nitric acid or potassium permanganate cause conversion into sulphuric acid with the intermediate formation of sulphur. The reaction is quantitative with a mixture of potassium chlorate and hydrochloric acid.⁹

The Pentathionates.—These salts are unstable, and even those of the alkali metals are so difficult to prepare ¹⁰ as to arouse a sugges-

¹ Josephy, *Zeitsch. anorg. Chem.*, 1924, 135, 21.

² Gripon, *Compt. rend.*, 1863, 56, 1137; Myers, *J. prakt. Chem.*, 1869, 108, 23.

³ Brugnatelli and Pelloggio, *Ber.*, 1875, 8, 71.

⁴ Kessler, *Ann. Phys. Chem.*, 1848, [ii.], 74, 249; Debus, *loc. cit.*

⁵ Berthelot, *Compt. rend.*, 1889, 108, 775; Thomsen (*Ber.*, 1873, 6, 555) gives 183 Cals.

⁶ Hertlein, *Zeitsch. physikal. Chem.*, 1896, 19, 302.

⁷ Riesenfeld and Feld, *Zeitsch. anorg. Chem.*, 1921, 119, 225; Foerster and Hornig, *ibid.*, 1922, 125, 86; Kurtenacker and Kaufmann, *ibid.*, 1925, 148, 43.

⁸ Debus, *loc. cit.*

⁹ Raschig, *loc. cit.*

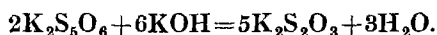
¹⁰ Kessler, *Ann. Phys. Chem.*, 1848, [ii.], 74, 249; *Annalen*, 1880, 200, 256; Ludwig, *ibid.*, 1844, 51, 259; Curtius, *J. prakt. Chem.*, 1881, [ii.], 24, 225; 1888, 37, 137; Berthelot,

tion¹ that the acid $\text{H}_2\text{S}_5\text{O}_6$ had no real existence and that the so-called pentathionic acid was a colloidal solution of sulphur in aqueous tetrathionic acid. The definite existence of the acid was finally proved by the isolation of solid pentathionate by the cautious addition of a solution of hydroxide of barium or potassium to excess of the acid solution, when the tetrathionate crystallised first, followed by a deposit of pentathionate.² In order to avoid further the harmful action of alkali on the free acid, Debus used the acetates of the metals in place of the hydroxides and recrystallised the pentathionate from water containing a little sulphuric acid.³ As potassium pentathionate is less dense than potassium tetrathionate, whilst a mixture of bromoform and xylene of specific gravity 2.2 has an intermediate density, it has been found possible to separate the potassium salts by addition of this liquid mixture, when the tetrathionate sinks and the pentathionate rises to the surface.⁴

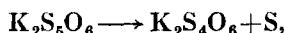
The pentathionates are not stable, decomposing spontaneously alone or in aqueous solution with gradual formation of tetrathionate, tri-thionate and sulphur, the change being retarded by the addition of a little hydrochloric or sulphuric acid. When heated in the dry condition they yield sulphate, sulphur and sulphur dioxide :



Hot alkaline solutions cause the pentathionates to undergo rapid conversion into thiosulphate, whilst with cold solutions some free sulphur is deposited, a corresponding amount of sulphite being produced, together with the thiosulphate :⁵

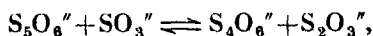


Sodium carbonate causes deposition of sulphur and formation of tetrathionate :



but the reaction is not quantitative as stated by Raschig,⁶ and also proceeds beyond this stage.

Sulphites⁷ give tetra- and tri-thionates and thiosulphate,



the decomposition of the tetrathionate proceeding as already described.⁸ The reaction with bisulphites is similar, tetrathionate first being produced (see p. 216).

The action of hydrogen sulphide and of sulphur dioxide has already received mention under the description of the acid.

Compt. rend., 1889, 108, 926; Stengl and Morawski, *Ber.*, 1879, 12, 2018; Smith and Takamatsu, *Trans. Chem. Soc.*, 1880, 37, 592; 1882, 41, 162; Fordos and Gélis, *Ann. Chim. Phys.*, 1848, [iii.], 22, 66; 1850, [iii.], 28, 451.

¹ Spring, *Annalen*, 1879, 197, 116; 1882, 213, 329. See also Lewes, *Trans. Chem. Soc.*, 1881, 39, 68; Valetton, *Chem. Weekblad*, 1907, 4, 553.

² Lewes, *loc. cit.*; Shaw, *Trans. Chem. Soc.*, 1883, 43, 351.

³ Debus, *loc. cit.*

⁴ Hertlein, *Zeitsch. physikal. Chem.*, 1896, 19, 293.

⁵ Kurtenacker and Kaufmann, *Zeitsch. anorg. Chem.*, 1925, 148, 369.

⁶ Raschig, *loc. cit.* See Kurtenacker and Czernotzky, *Zeitsch. anorg. Chem.*, 1928, 174, 179.

⁷ For the detection of small amounts of pentathionate in the presence of sulphites, see Czernotzky, *Zeitsch. anorg. Chem.*, 1928, 175, 402.

⁸ Foerster and Centner, *ibid.*, 1926, 157, 45.

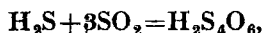
Potassium amalgam reduces an aqueous pentathionate solution to tetrathionate and thiosulphate. Metallic copper and silver are blackened by pentathionate solutions.

"Wackenroder's Solution."

Whenever sulphur dioxide, water and "nascent" sulphur meet, for example in the action of water on sulphur chloride, of mineral acids on a thiosulphate, or of hydrogen sulphide on aqueous sulphur dioxide solution, formation of polythionic acids is likely to occur. Dalton¹ in 1812 demonstrated that the last-named reagents gave rise to an acid liquid, a result which was confirmed later by Thomson;² in 1846 Wackenroder³ proved the presence of pentathionic acid in the liquid, since which date the aqueous reaction product has been known as "Wackenroder's Solution."

The reaction was subsequently investigated by other chemists, particularly Debus,⁴ who found that the most satisfactory procedure was to treat an almost saturated cold solution of sulphur dioxide repeatedly with hydrogen sulphide on successive days until the sulphur dioxide was consumed. The resulting liquid contained sulphur in colloidal suspension, free sulphur (see also p. 80), sulphuric acid, a little trithionic acid, tetrathionic acid and pentathionic acid, and an acid or acids still richer in sulphur—possibly a hexathionic acid.⁵

Examination of the progress of the reaction indicated that the first product is probably tetrathionic acid:



which subsequently undergoes partial decomposition by hydrogen sulphide with formation of water and sulphur; the sulphur, being in a "nascent" condition, converts some of the tetrathionate to pentathionate, whilst some of the tetrathionate also undergoes reduction to trithionate.

The composition of Wackenroder's solution varies with the conditions of preparation. When prepared in the manner described, the milky solution can be clarified by careful evaporation at the ordinary temperature in a vacuum, when the suspended sulphur separates and a solution containing mainly pentathionic acid is obtained.

The observed occurrence of pentathionic acid in natural waters⁶ is doubtless to be attributed to a reaction of this kind between sulphur dioxide and hydrogen sulphide.

Hexathionic Acid, $\text{H}_2\text{S}_6\text{O}_6$.—The potassium salt of this acid has been prepared⁷ by adding a solution containing potassium nitrite and potassium thiosulphate (1KNO_2 to $3\text{K}_2\text{S}_2\text{O}_3$) to well-cooled hydrochloric acid, the mixture being vigorously shaken until the colour

¹ Dalton, "*New System*," 1812.

² Thomson, *Phil. Mag.*, 1826, 12, 441.

³ Wackenroder, *Annalen*, 1846, 60, 189.

⁴ Debus, *Chem. News*, 1888, 57, 87. See also Hertlein, *Zeitsch. physikal. Chem.*, 1896, 19, 289; Lang and Carson, *Proc. Chem. Soc.*, 1905, 21, 158; Raschig, *Schwefel- und Stickstoff-Studien*, 1924, p. 273. See *Chem. Zeit.*, 1924, ii., 1065.

⁵ Weitz and Achterberg (*Ber.*, 1928, 61, [B], 399) report the absence of hexathionic acid but confirm the presence of acids richer in sulphur.

⁶ Maclaurin, *Proc. Chem. Soc.*, 1911, p. 10.

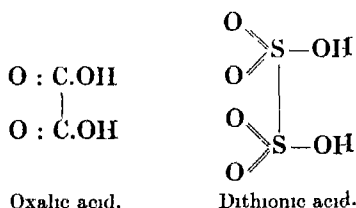
⁷ Weitz and Achterberg, *loc. cit.*; Partington and Tipler, *J. Chem. Soc.*, 1929, p. 1382.

changes through brown and green to yellow. Nitrous fumes are removed by passing air through the solution, which then has an odour of sulphur dioxide. On keeping in a freezing mixture potassium chloride separates and the solution becomes almost colourless. After filtration and concentration under reduced pressure, potassium hexathionate contaminated with potassium chloride separates; the latter is removed by water and the hexathionate washed with alcohol and ether. Potassium tetrathionate is contained in the mother-liquor, its formation probably being due to the intermediate formation of nitrosylthiosulphuric acid, but the mechanism of the reaction is obscure.

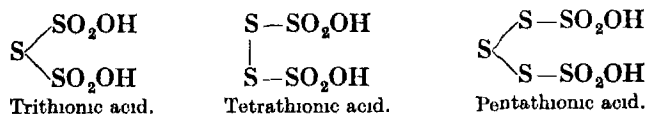
Potassium hexathionate is stable when dry, but in aqueous solution undergoes decomposition with formation of sulphur or a higher polythionate. The addition of acid stabilises the solution, and the salt is best crystallised from solutions containing considerable amounts of mineral acid; from such solutions it may be salted out. It resembles the pentathionates in its reaction with alkalis and with sodium carbonate, sulphur being deposited; also in giving no precipitate with copper sulphate. It gives a yellow precipitate with mercurous nitrate, a yellowish-white precipitate with mercuric chloride, and a brown coloration followed by a black precipitate with ammoniacal silver nitrate. It is decomposed by aqueous ammonia, the primary product being tetrathionate; the reaction is more rapid than in the case of pentathionates. Sulphites produce trithionates. Hexamine-cobaltic and -chromic chlorides and nitrates give crystalline precipitates.

Hexathionic acid itself is as yet unknown.

The Constitution of the Polythionic Acids.—The earliest suggestions as to the constitution of these acids represented dithionic acid as a sort of sulphur analogue to oxalic acid,



and the higher thionic acids as derived from dithionic acid by the interposition of sulphur atoms between the sulphonic acid groups :¹



According to this view the intermediate sulphur atoms are probably arranged in a similar manner in the polythionic acids and the hydrogen polysulphides, and tetrathionic acid may be considered as a sulphur analogue to perdisulphuric acid.²

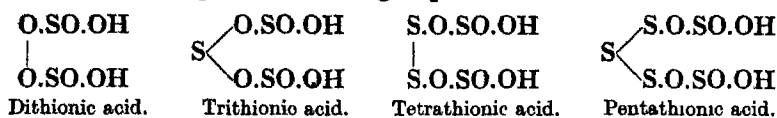
Alternative structures were suggested by Michaelis,³ who regarded

¹ Blomstrand, *Chemie der Jetztzeit*, pp. 157, 257 (Heidelberg, 1869); Mendeléeff, *Ber.*, 1870, 3, 870. See also Hertlein, *Zetsch. physikal. Chem.*, 1896, 19, 310; Colofax, *Trans. Chem. Soc.*, 1908, 93, 881.

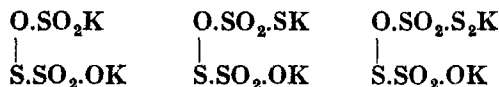
² Calzolari, *Atti R. Accad. Lincei*, 1915, [v.], 24, i., 921.

³ Michaelis, *Annalen*, 1873, 170, 31. See also Pascal, *Compt. rend.*, 1921, 173, 712.

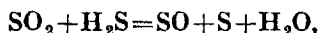
the polythionic acids as constituting anhydride derivatives of sulphurous acid and containing the terminal groups $-\text{O}.\text{SO}.\text{OH}$, thus :



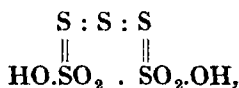
Debus¹ favoured the assumption that the central linking atoms between the terminal acidic groups comprise an oxygen and a sulphur atom :



Raschig² considered the formation of pentathionic acid in "Wackenroder's solution" to be due to the condensation of five SO-groups arising from the reaction



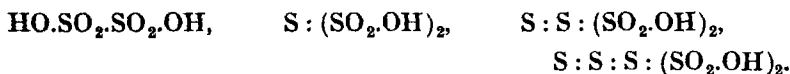
the addition of water resulting in the arrangement



the lower acids being formulated



Vogel,³ in order to explain the formation of the tri-, tetra- and pentacids from sulphur sesquioxide, the liberation of two atoms of sulphur from pentathionates by bromine, and other reactions, suggested the formulæ :



The complex nature of the process of decomposition of these acids and their behaviour on oxidation makes it difficult to decide which of the foregoing formulæ are most satisfactory for the tetra- and pentathionic acids. In the case of dithionic and trithionic acids, the formulæ given by Blomstrand and Mendeléeff and by Vogel appear to accord best with the general behaviour of the acids.

More recently Christiansen⁴ has made a careful study of the polythionic acids and especially of certain physical properties—K-radiations, electrical moments, and molecular weights by ebullioscopic methods—of the *p*-toluoyl-tri-, -penta- and -hexa-thionates, and suggests that none of the foregoing formulæ is adequate, but that the properties and reactions of the acids are best explained by the assumption that the

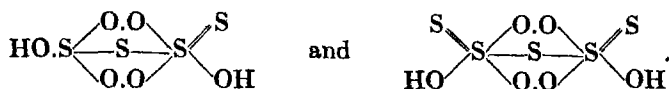
¹ Debus, *loc. cit.* See also Gutmann, *Ber.*, 1905, 38, 1728, 3277.

² Raschig, *loc. cit.* See also Foerster, *Zeitsch. anorg. Chem.*, 1924, 141, 228.

³ Vogel, *Chem. News*, 1924, 128, 325, 342; *Trans. Chem. Soc.*, 1925, 127, 2248.

⁴ Christiansen, *Zeitsch. Elektrochem.*, 1928, 34, 638; *Forh. III nord. Kemistmötet*, 1928, p. 177.

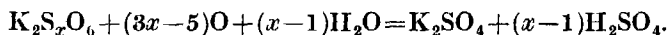
molecules contain a six-membered ring. Thus, the tetra- and pentathionic acids may be respectively formulated as



The bimolecular nature of sulphur trioxide is cited in support of these views, and the absence of colour in the polythionic acids is mentioned as being opposed to the polysulphide linking of some of the earlier formulæ. Nevertheless, the above formulæ do not appear to be in agreement with the relative stabilities of the acids, but suggest that the tetrathionic acid is less stable than the more compact trithionic acid, or than the more saturated pentathionic acid (*cf.* pp. 211, 215).

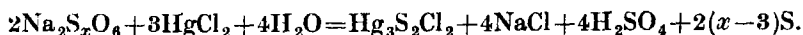
Co-ordination formulæ have also been suggested.¹

Estimation.—The usual procedure with the polythionates is to apply some convenient decomposition reaction. Oxidation is a convenient method, for example by aqua regia or a mixture of potassium chlorate, hydrochloric acid and bromine; the amount of sulphuric acid resulting gives an indication of the quantity of sulphur present in the original polythionate: ²



An attractive modification of this method is to treat the neutralised polythionate solution with neutral hydrogen peroxide and a known excess of standard sodium hydroxide solution on the water-bath and to determine the quantity of acid formed by the amount of standard alkali neutralised during the oxidation.³ All polythionates except the dithionates are completely oxidised to sulphate by heating in a closed tube for one hour with iodine and sodium bicarbonate; by titrating the excess of iodine the total polythionate present may be estimated.⁴

An alternative method is based on the interaction of mercuric chloride with polythionates in aqueous solution. A white precipitate of the mercuric thiochloride already mentioned under thiosulphuric acid ⁵ is formed; the equation is



This method is especially suited to the trithionates and tetrathionates, and is applicable even in the presence of thiosulphate or sulphite by first titrating the neutral solution with iodine, which indicates the total quantity of sulphite and thiosulphate, and then determining the acidity developed during the iodine titration, from which the amount of sulphite can be calculated. Finally the mercuric chloride reaction is applied to another portion of the original solution and by determination

¹ Martin and Metz, *Zeitsch. anorg. Chem.*, 1923, 127, 83.

² For variations of this principle, see Ashley, *Amer. J. Sci.*, 1906, [iv.], 22, 259; Baubigny, *Compt. rend.*, 1909, 149, 1069; Jamieson, *Amer. J. Sci.*, 1915, 39, 639.

³ Lang and Carson, *Proc. Chem. Soc.*, 1905, p. 159; Calzolari, *Gazzetta*, 1910, 40, ii., 22; Sander, *Zeitsch. angew. Chem.*, 1916, 29, 11, 16.

⁴ Riesenfeld and Sydow, *Zeitsch. anorg. Chem.*, 1928, 175, 74.

⁵ Sander, *Zeitsch. angew. Chem.*, 1915, 28, 9; 1916, 29, 11, 16. See also Feld, *ibid.*, 1913, 26, 286; 1911, 24, 290; Kurtenacker and Bittner, *Zeitsch. anorg. Chem.*, 1925, 142, 119.

of the acidity developed and allowing for the effect of the sulphite and thiosulphate (q.v.), the amount of polythionate is calculated.¹

Sulphur Sesquioxide, S_2O_3 .

Buchholz² in 1804 observed that fuming sulphuric acid could dissolve finely divided sulphur, giving an unstable blue solution. In 1812 Vogel³ obtained the coloured substance by the direct addition of sulphur to liquid sulphur trioxide at the ordinary temperature; drops of a bluish-green liquid separated, which solidified in crusts. The main excess of trioxide was drained away, complete removal being effected by careful evaporation⁴ near 38°C . By the addition of liquid sulphur trioxide to finely powdered sulphur, instead of *vice versa*, the product is more easily obtainable.⁵

The bluish-green crystalline mass is very unstable and decomposes fairly rapidly even at the ordinary temperature, giving sulphur dioxide and sulphur. The pure substance may be preserved for several hours in a vacuum. It is hygroscopic, and on absorbing moisture first becomes brown and then deposits sulphur, with concurrent formation of sulphur dioxide, sulphuric acid and possibly other sulphur acids. It is soluble in fuming sulphuric acid, an acid rich in trioxide giving a bluish solution, whilst with less rich acids the solution is brown; ordinary pure sulphuric acid causes decomposition. The colour of the brown solution is regarded by some as due to colloidal sulphur formed by partial decomposition of the sesquioxide.⁶

Nitric acid or bromine causes rapid oxidation of the oxide, which may be accompanied by explosion. Pure dry ether also reacts violently, with separation of sulphur and formation of a yellow solution which, on evaporation, yields a yellow oil. Absolute alcohol acts similarly.

The composition of the oxide suggests that it may be an acid anhydride, but all attempts to convert it into hydrosulphurous acid, $H_2S_2O_4$, or its derivatives, have been unsuccessful.⁷

Analogous oxides are known containing one atom of sulphur replaced by selenium or tellurium. The tellurium compound, *tellurium sulphoxide*, $STeO_3$, decomposes with production of tellurium monoxide, TeO , when gradually heated in a vacuum to 225°C .⁸ Attempts to produce sulphur monoxide similarly from sulphur sesquioxide have not been successful.

An application has been suggested for this sesquioxide in the preparation of certain organic dyes containing sulphur.⁹

¹ See also, for the determination of polythionates in the presence of other sulphur acids and of each other, Muller, *Bull. Soc. chim.*, 1916, [iv.], 19, 8; Billeter and Wavre, *Helv. Chim. Acta*, 1918, 1, 174; Kurtenacker and Fritsch, *Zeitsch. anorg. Chem.*, 1921, 117, 262; 1922, 121, 335; Fischer and Classen, *Zeitsch. angew. Chem.*, 1922, 35, 198; Riesenfeld, Josephy and Grunthal, *Zeitsch. anorg. Chem.*, 1923, 126, 281; Mayr and Szentpaly-Peyfuss, *ibid.*, 1924, 131, 203; Kurtenacker and Bittner, *loc. cit.*; Kurtenacker and Goldbach, *Zeitsch. anorg. Chem.*, 1927, 166, 177; Riesenfeld and Sydow, *ibid.*, 1928, 175, 74; Terres and Overdick, *Gas- u. Wasserfach*, 1928, 71, 49, 81, 106, 130.

² Buchholz, *Gehlen's J. Chem.*, 1804, 3, 7.

³ Vogel, *Schweigger's J.*, 1812, 4, 121.

⁴ Weber, *Ann. Phys. Chem.*, 1875, [ii.], 156, 531.

⁵ Vogel and Partington, *Trans. Chem. Soc.*, 1925, 127, 1514.

⁶ Biehringer and Topalov, *J. prakt. Chem.*, 1902, 65, [2], 499; Stein, *ibid.*, 1838, 6, 172.

⁷ See Vogel and Partington, *loc. cit.*

⁸ Divers and Shimose, *Ber.*, 1883, 16, 1009; Doolan and Partington, *Trans. Chem. Soc.*, 1924, 125, 1403.

⁹ Biehringer and Topalov, *loc. cit.*

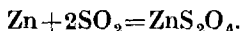
Hydrosulphurous Acid, $\text{H}_2\text{S}_2\text{O}_4$.

Schönbein in 1852–1858, during a re-investigation of the electrolysis of sulphurous acid solution, examined about twenty years before by Faraday, obtained at the cathode a yellowish solution of marked reducing power; he obtained a solution of similar properties on treatment of sulphurous acid solution with zinc,¹ which reaction was already known from the observations of Berthollet, Fourcroy and Vauquelin to give no free hydrogen.

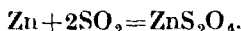
A further examination of the action of zinc on sulphurous acid and on sodium hydrogen sulphite solutions was made by Schützenberger² in 1869, who arrived at a formula NaHSO_2 for the sodium salt, and suggested the name *hydrosulphurous acid*; although the formula has proved to be incorrect, the name possesses an advantage in precluding any confusion with thiosulphuric acid; the possibility of such confusion is introduced by the term *hyposulphurous acid*, which, however, until recent years, received fairly general acceptance in English-speaking countries. Under the present system of nomenclature “hyposulphurous acid” should be H_2SO_2 , which, however, is termed sulphoxylic acid.

The free acid is exceedingly unstable and cannot be isolated, only the salts being of importance. These may be obtained as follows:

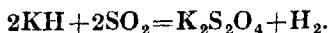
Zinc slowly dissolves in sulphurous acid solution without effervescence; the solution is at first yellow and then becomes colourless; air should be excluded. The action probably follows the course³



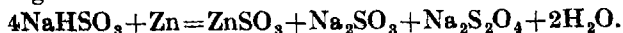
It is possible to prepare the hydrosulphites of the metals in anhydrous condition by the action of various metals, for instance zinc, magnesium, sodium, on sulphur dioxide in the presence of moisture-free ether⁴ or alcohol.⁵ This reaction is of importance as having supplied an early proof of the absence of hydrogen from the salts and hence of the incorrectness of the formulae $\text{Zn}(\text{HSO}_2)_2$, NaHSO_2 , which had been accepted previously:



Moissan in 1902 obtained anhydrous hydrosulphites by passing sulphur dioxide diluted with hydrogen over the hydrides of the alkali and alkaline earth metals.⁶ He was able to produce the hydrosulphites of sodium, potassium, lithium, calcium and strontium in this way, and by measurement of the quantity of hydrogen liberated was able to prove the correctness of the general formula $\text{M}_x\text{S}_2\text{O}_4$:



Sodium hydrogen sulphite solution⁷ can be used in place of the aqueous sulphurous acid in the first method described. With zinc, the resulting reaction is



¹ See Schär, *Ber.*, 1894, 27, 2714.

² Schützenberger, *Compt. rend.*, 1869, 60, 196; *Bull. Soc. chim.*, 1873, [ii.], 19, 152; 20, 145.

³ Bernthsen, *Annalen*, 1881, 208, 142; Causse, *Bull. Soc. chim.*, 1886, 45, 3.

⁴ Nabl, *Monatsh.*, 1899, 20, 679.

⁵ Billy, *Compt. rend.*, 1905, 140, 938.

⁶ Moissan, *Compt. rend.*, 1902, 135, 647.

⁷ Schützenberger, *loc. cit.*; Causse, *loc. cit.*

The result is more satisfactory if the acid sulphite is accompanied by a semi-molecular proportion of sulphurous acid :



On pouring the solution into alcohol a double sulphite of sodium and zinc is rapidly precipitated, whilst needles of sodium hydrosulphite, $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, separate slowly afterwards. Another procedure for the removal of the zinc from the solution is to add milk of lime cautiously, when a solution of sodium hydrosulphite remains.¹

Other metals may be used in place of zinc, *e.g.* iron, copper, manganese² or even sodium amalgam or calcium.³

In the electrolysis of aqueous sulphurous acid or sodium hydrogen sulphite solution, a little hydrosulphite is formed at the cathode as a result of the reduction process.⁴

Titanous chloride also reduces sulphurous acid or sodium hydrogen sulphite solution with formation of an orange-yellow solution of hydrosulphurous acid,⁵ from which sodium hydrosulphite is obtainable by further treatment with sodium hydroxide solution :



Formic acid,⁶ when mixed with aqueous sodium hydrogen sulphite, forms a solution of strong reducing power, due to conversion of some of the sulphite by reduction into hydrosulphite :



Sodium formaldehydesulphoxylate (see p. 228) may be used conveniently instead of formic acid.⁷

Hydrosulphurous acid is also formed as an intermediate product in the reduction of sulphurous acid by hypophosphorous acid.⁸

The free acid is exceedingly unstable, and its orange-yellow aqueous solution, obtained directly by any of the methods already described, or by decomposition of a hydrosulphite with a suitable acid such as dilute sulphuric acid, is capable only of short existence, soon decomposing with deposition of sulphur and liberation of sulphurous acid⁹ (see p. 231). By measurement of the electrical conductivity of solutions of the acid and of the sodium salt it has been possible to show that hydrosulphurous acid is a stronger acid than sulphurous acid, although weaker than thiosulphuric acid.¹⁰ According to Berthelot the heat of formation of the acid in aqueous solution is a small positive quantity.¹¹

Details of the strong reducing character of the acid will be found in the following, under the description of the reactions of the hydrosulphites.

¹ Bazlen, *Ber.*, 1905, 38, 1057.

² Causse, *loc. cit.*

³ Grandmougin, *Bull. Soc. Ind. Mulhouse*, 1906, 76, 351.

⁴ Schützenberger, *loc. cit.*; Guerout, *Compt. rend.*, 1877, 85, 225; Jellinek, *Zeitsch. Elektrochem.*, 1911, 17, 245; Meyer, *Zeitsch. anorg. Chem.*, 1903, 34, 43, Ekker, *Rec. Trav. chim.*, 1895, 14, 57; Muller, *Zeitsch. Elektrochem.*, 1904, 10, 776.

⁵ Spence and Knecht, *German Patent*, 141452 (1903).

⁶ Kapff, *German Patent*, 175582 (1905). See also *German Patent*, 436997 (1924).

⁷ Heyl and Greer, *Amer. J. Pharm.*, 1922, 94, 80.

⁸ Maquenne, *Bull. Soc. chim.*, 1890, [iii.], 3, 401.

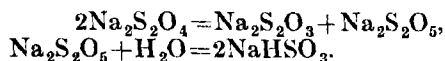
⁹ Meyer, *Zeitsch. anorg. Chem.*, 1903, 34, 43.

¹⁰ Jellinek, *Zeitsch. physikal. Chem.*, 1911, 76, 257.

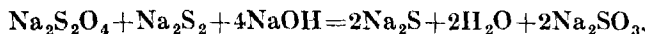
¹¹ Berthelot, *Compt. rend.*, 1876, 83, 418.

The Hydrosulphites.—These salts are much more stable than the free acid; the best known salts are those of the alkali and the alkaline earth metals, for example $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{K}_2\text{S}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$, $\text{CaS}_2\text{O}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$.¹ As will be seen from these formulæ, the acid is dibasic, but only normal salts are known. The zinc salt is also fairly stable, especially in the form of double salts with the alkali hydrosulphites, for example $\text{Na}_2\text{Zn}(\text{S}_2\text{O}_4)_2$.¹ Crystalline hydrosulphites of aromatic amines have also been obtained by interaction of the sodium salt with the hydrochloride of the amine.²

The hydrated salts obtained by ordinary crystallisation from water are relatively unstable, and tend in the solid condition or in aqueous solution with exclusion of air to decompose into thiosulphate and sulphite (the latter as pyrosulphite or acid sulphite, according to the conditions);³ the further interaction of these primary products complicates the final result. In the case of the sodium salt in aqueous solution the reaction is bimolecular and follows the scheme⁴



In the presence of alkali, hydrosulphites react with alkali polysulphides with the formation of sulphite and sulphide:



a similar result being obtained with thiosulphates, although more slowly:⁵



As reducing agents the hydrosulphites are exceptionally active and generally become oxidised to sulphites, although with relatively strong oxidising agents such as hydrogen peroxide or iodine, sulphate⁶ may be formed.

Ferric salts are reduced to the ferrous condition and chromates are reduced to chromic salts. Salts of gold, silver, copper, antimony, bismuth and mercury are reduced to the free metals, which are frequently obtained as colloidal solutions if the original solutions are weak; with the exception of the first-named there is a tendency for the liberated metal to be accompanied by sulphide, especially if excess of hydrosulphite is used.⁷ Chloroplatinic acid is reduced to red chloroplatinous acid solution. Tellurous and telluric acids, selenous acid and arsenic compounds, are reduced to the free elements.⁸

Indigo and many other colouring matters are bleached by sodium hydrosulphite.⁹ Organic nitro-compounds are reduced to amino-compounds, the group $-\text{NO}_2$ being converted into $-\text{NH}_2$.¹⁰

¹ Bazlen, *Ber.*, 1905, 38, 1057; Meyer, *loc. cit.*

² Lumière, Lumière and Seyewetz, *Bull. Soc. chim.*, 1905, [iii.], 33, 67.

³ Meyer, *loc. cit.*

⁴ Jellinek, *Zeitsch. physikal. Chem.*, 1919, 93, 325.

⁵ Binz, *Ber.*, 1905, 38, 2051; Binz and Sondag, *ibid.*, 1905, 38, 3830.

⁶ Meyer, *loc. cit.*; Bernthsen, *Ber.*, 1881, 14, 439.

⁷ For example, see reduction of CuCl_2 , Firth and Higson, *Trans. Chem. Soc.*, 1923, 123, 1515.

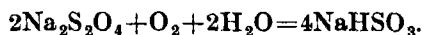
⁸ Meyer, *loc. cit.*; Brunck, *Annalen*, 1904, 336, 281.

⁹ Schär, *Ber.*, 1894, 27, 2714; Kuhlmann, *Compt. rend.*, 1855, 41, 538; Eymer, *Rev. gén. Mat. Col.*, 1925, 39, 96.

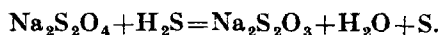
¹⁰ For further use in the reduction of organic compounds, see Bucherer, *German Patent*, 423029 (1922).

Anhydrous hydrosulphites are obtained as products of methods described on p. 225. Commercially the anhydrous sodium salt is manufactured in large quantities on account of its greater stability than the hydrated $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The latter can be dehydrated by extraction with warm alcohol or acetone at 60° to 70° C. It is also possible to produce the anhydrous salt directly by precipitation of the aqueous solution with alcohol at 60° to 70° C., or even by "salting out" the solution at this temperature by the addition of sodium hydroxide, chloride, sulphate, carbonate, nitrate or acetate; with sodium hydroxide solution of 50 per cent. concentration the anhydrous salt can be separated even at 20° C.¹

The hydrosulphites are very liable to atmospheric oxidation, especially in the hydrated or moist condition; in their preparation and preservation it is therefore desirable to exclude air. When exposed to the atmosphere a solution of a hydrosulphite first becomes yellow, probably due to the transient presence of free hydrosulphurous acid, but soon becomes colourless, the final product being sulphite.² Much heat is evolved during this oxidation, as may readily be observed with the exposed moistened salt:



With hydrogen sulphide the aqueous solution reacts with formation of thiosulphate and sulphur,³ the equation being



In feebly acid solution the salts of such metals as nickel, cobalt, lead, zinc and cadmium react with hydrosulphites yielding the corresponding metal sulphide and no free metal.⁴

With aldehydes and ketones sodium hydrosulphite readily forms additive compounds, the most important being that derived from formaldehyde.⁵ This product appears to have the composition $2\text{CH}_2\text{O} \cdot \text{Na}_2\text{S}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$, but is separable by recrystallisation from water into the sodium hydrogen sulphite derivative of formaldehyde, viz. $\text{CH}_2\text{O} \cdot \text{NaHSO}_3 \cdot \text{H}_2\text{O}$, and an analogous compound $\text{CH}_2\text{O} \cdot \text{NaHSO}_2 \cdot 2\text{H}_2\text{O}$,⁶ a crystalline solid of m.pt. 63° to 64° C. The latter is known as "Rongalite" and is of especial commercial importance on account of its stability at the ordinary temperature, although at steam heat it exerts all the reducing power of the hydrosulphites; on this account "Rongalite," or sodium formaldehydesulphoxylate (p. 102), is a very convenient

¹ Bazlen, *loc. cit.*; Jellinek, *Zetsch. anorg. Chem.*, 1911, 70, 93, 71, 96. For a method of obtaining $\text{Na}_2\text{S}_2\text{O}_4$ of 98 per cent. purity from the commercial product by a salting out method, see Christiansen and Norton, *J. Ind. Eng. Chem.*, 1922, 14, 1126. See also Badische Anilin- und Soda-Fabrik, *German Patents*, 160529, 171991, 172929, etc. (1905); also *U.S. Patent*, 1609773 (1926).

² Schützenberger, *Compt. rend.*, 1869, 69, 196; Meyer, *loc. cit.*

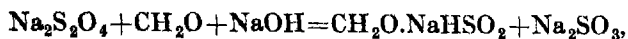
³ Sinnatt, *J. Soc. Dyers*, 1914, 30, 189.

⁴ Orloff, *J. Russ. Phys. Chem. Soc.*, 1904, 36, 1311.

⁵ Bazlen, *Ber.*, 1905, 38, 1057; Siegmund, *Monatsh.*, 1912, 33, 1431; Meister, Lucius and Brünig, *German Patent*, 162875 (1906).

⁶ Baumann, Thesmar and Frossard, *Bull. Soc. Ind. Mulhouse*, 1904, 74, 348; Schmid, *ibid.*, 1904, 74, 63; Zundel, *ibid.*, 1904, 74, 49; Prud'homme, *Bull. Soc. chim.*, 1905, [iii.], 33, 129; Reinking, Dehnelt and Larhardt, *Ber.*, 1906, 38, 1069; Binz and Isaac, *ibid.*, 1908, 41, 3381; Binz and Marx, *ibid.*, 1910, 43, 2344, 2350.

form of reducing agent where storage for prolonged periods may be necessary before use. The aqueous solution may be stabilised by addition of a soluble zinc salt. Various other methods have been recommended for the preparation of "Rongalite," for example, the interaction of hydrosulphite and formaldehyde in the presence of an alkali :



and the reduction of sodium hydrogen sulphite solution with zinc dust and zinc oxide in the presence of formaldehyde,¹ recrystallising from water at a temperature not exceeding 70° C. the crystals first obtained.

Applications.—Sodium hydrosulphite and sodium formaldehyde-sulphoxylate ("Rongalite") are largely applied industrially, generally for bleaching purposes. Sugar,² soap, straw, etc., can be improved in colour by treatment with these reagents. In the dyeing industry also these substances are used, for example to convert insoluble dyes like indigo into a soluble form, by which means a vat suitable for dyeing can be obtained; the reducing agent may also be applied locally to a dyed cloth and a pattern thereby produced.

Constitution.—Although the formation of sodium formaldehyde-sulphoxylate from sodium hydrosulphite (see before) might appear to indicate that the latter is a mixture of sodium hydrogen sulphite with sodium hydrogen sulphoxylate, NaHSO_2 , it is generally accepted that the hydrosulphites are definite compounds;³ a simple experimental observation in favour of this view is that a slightly alkaline solution of sodium hydrosulphite becomes acid on atmospheric oxidation, whereas an alkaline solution of sodium sulphite and sodium sulphoxylate should produce only normal sulphite and sulphate.⁴ The *sulphoxylates* are little known except for their formaldehyde derivatives,⁵ only the sodium and zinc salts having been prepared (see p. 102). Except under exceptional conditions, therefore, the hydrosulphites are much more stable than the sulphoxylates.

Schützenberger⁶ ascribed to sodium hydrosulphite the formula NaHSO_2 which, curiously enough, was also one of the earliest formulæ suggested for sodium thiosulphate.⁷ Oxidation processes are of assistance in indicating the nature of hydrosulphurous acid; thus when oxidised to the stage of sulphite, for example by ammoniacal copper sulphate solution, one atomic weight of oxygen is required per molecule of acid, whilst on oxidation to the stage of sulphate, which can be effected by iodine or by ammoniacal copper sulphate with the addition of ammonium chloride, a total of three atomic weights of oxygen is consumed; these results accord with the following equations :

¹ Schwarz, *Bull. Soc. chim.*, 1900, 73, 183; Chem. Fabrik von Heyden, *German Patents*, 202825, 202826, 202827 (1909); Heyl and Greer, *Amer. J. Pharm.*, 1922, 94, 80.

² Englert and Becker, *Dingl. poly. J.*, 1886, 262, 186.

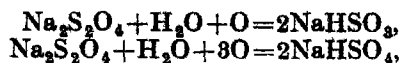
³ Bernthsen, *Ber.*, 1881, 14, 438, 2228; 1882, 15, 921; 1905, 38, 1048.

⁴ Binz, *Zeitsch. Farb. Text. Ind.*, 1905, 4, 161.

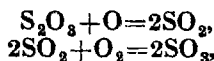
⁵ Fromm, *Ber.*, 1906, 39, 3317; 1908, 41, 3397. For the preparation of calcium derivatives, see Johnson, *British Patent*, 281134 (1927).

⁶ Schützenberger, *Bull. Soc. chim.*, 1869, [ii.], 12, 123; 1873, [ii.], 19, 152; 20, 145.

⁷ Odling, *Trans. Chem. Soc.*, 1869, 22, 180 ($2\text{NaHSO}_2 = \text{Na}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$).



or

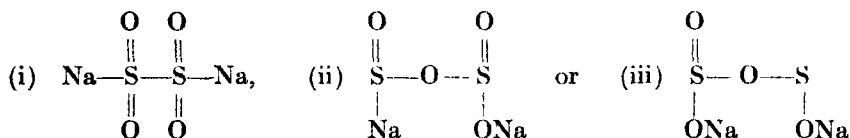


according to which hydrosulphurous acid corresponds with an oxide S_2O_3 (see, however, p. 224), whereas the oxide required for a salt NaHSO_2 would be SO . In this way a decision between the formulæ NaHSO_2 and $\text{Na}_2\text{S}_2\text{O}_4$ is easily made, whereas the percentage of sodium and sulphur in the two salts is almost the same and is of relatively little value in enabling a selection between the two to be made.

Confirmatory evidence of the probable correctness of the formula $\text{Na}_2\text{S}_2\text{O}_4$ is supplied by electrical conductivity measurements on aqueous solutions and comparison of the results with those given by the normal salts of the other sulphur oxy-acids, namely Na_2SO_4 , Na_2SO_3 , $\text{Na}_2\text{S}_2\text{O}_3$ and $\text{Na}_2\text{S}_x\text{O}_6$. All these salts dissociate in two stages. Cryoscopic measurements with the sodium salt also indicate the formation of three ions per molecule.

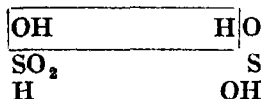
The foregoing considerations were of especial importance in the earlier history of the hydrosulphites, before the salts had been obtained in a pure condition and before their syntheses by the direct interaction of sulphur dioxide and the metal or metallic hydride were available as evidence.

Considering sodium hydrosulphite instead of the unisolated free acid, the constitution is probably to be represented by one of the following formulæ:



The direct sulphur to sulphur linking in the first formula is in harmony with the formation of the salt by reduction of the sulphite and with the stability of the salt in the presence of alkalis,¹ but it is discounted by the absence of dithionate from the oxidation products, and by the easy fission of the substance into sulphite and sulphonylate on treatment with an aldehyde.

The formulæ² containing the $\text{S}-\text{O}-\text{S}$ chain are in accordance with the assumption that the acid is a mixed anhydride derived from sulphonylic and sulphurous acids:



In support of this contention, the hydrolysis of the sodium salt in

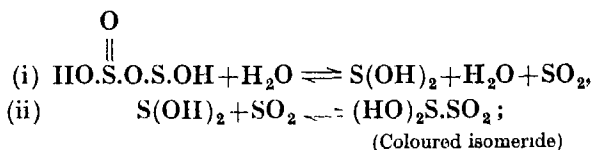
¹ Meyer, *Zeitsch. anorg. Chem.*, 1903, 34, 43; Jellinek, *ibid.*, 1911, 70, 93; 71, 96. See also Bazlen, *Ber.*, 1927, 60, [B], 1470; Raschig, *Schwefel- und Stickstoff-Studien*, 1924, p. 242; *Chem. Zentr.*, 1924, ii., 1093.

² Bernthsen and Bazlen, *Ber.*, 1900, 33, 126; Bernthsen, *ibid.*, 1905, 38, 1048; Bazlen, *ibid.*, 1905, 38, 1067; Binz, *ibid.*, 1904, 37, 3549; 1909, 42, 381.

alkaline solution in the presence of sodium plumbite may be cited; ¹ at room temperature lead sulphide and lead are slowly precipitated, but if the solution is boiled before the addition of the plumbite only the sulphide is precipitated. The reaction in the cold is similar to that of formaldehydesulphoxylate under similar conditions, so that sulphoxylate is evidently a product of the hydrolysis of the hydrosulphite. When the solution is boiled the sulphoxylate is decomposed, being converted into sulphide and sulphite as fast as it is formed. The presence of the S—O—S chain is also in agreement with the formation of benzyl sulphoxide, benzyldisulphonic acid and benzyldisulphinic acid ² on treatment with benzyl chloride and potassium hydroxide, and the only important fact possibly at variance with this constitutional representation is the stability of the substance towards alkalis, since it might be expected that a substance of such structure would resemble an acid anhydride in properties.

The third formula perhaps expresses the general behaviour of hydrosulphites more closely than the second, particularly with respect to the action with various oxidising agents. With mild oxidising agents sulphite is the main product, but gaseous oxygen is exceptional in producing approximately equivalent quantities of sulphate and sulphite.³

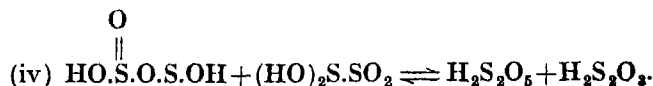
Aqueous solutions of hydrosulphites become orange-yellow on acidification and the presence of sulphur dioxide is soon evident. The yellow colour is not due to colloidal sulphur, nor, since its salts are colourless, would it be expected that the free acid should be yellow, unless there is some change in constitution. It has therefore been suggested ⁴ that the decomposition on acidification involves the formation of a coloured isomeride of the type (HO)₂S.SO₂ by co-ordination of a molecule of sulphur dioxide with the sulphur atom of sulphoxylic acid. The decomposition may proceed thus :



and/or



Further action results in the formation of pyrosulphite and thiosulphate,⁵ which may be explained thus :



¹ Bassett and Durrant, *J. Chem. Soc.*, 1927, p. 1403.

² Fromm and Palma, *Ber.*, 1906, 39, 3317.

³ Meyer, *loc. cit.*

⁴ Bassett and Durrant, *loc. cit.*

⁵ K. Jellinek and E. Jellinek, *Zeitsch. physikal. Chem.*, 1919, 93, 325.

In addition, the further breaking down of these decomposition products results in the formation of polythionates.¹

Estimation.—As the chief value of hydrosulphites lies in their reducing power, the method of estimation frequently consists of a measurement of the amount of a standard indigo solution which can be reduced by the sample. Another method is to titrate with standard ammoniacal copper sulphate solution until the hydrosulphite is almost completely oxidised and then to complete the process using indigo-carmin as indicator.² Ammoniacal silver nitrate solution has also been suggested as oxidising agent, in which case it is convenient to weigh the silver produced.³

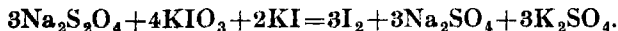
Instead of making a direct volumetric determination of the hydrosulphite it is possible to modify the process by estimating volumetrically the product of a primary reaction. For example the hydrosulphite solution may be submitted to atmospheric oxidation and the resulting acidity determined with standard alkali,² or a mercuric salt may be reduced, the mercury produced being estimated subsequently by the addition of standard iodine solution and titration of the excess of iodine; one molecule of hydrosulphite is equivalent to an atom of mercury and therefore to two atoms of iodine.⁴ Similarly, instead of the gravimetric estimation of silver as described above, the latter may be redissolved in nitric acid and determined volumetrically.⁵

Hydrosulphites may also be determined accurately by titration with standard ferricyanide⁶ solution using ferrous ammonium sulphate as indicator; the reaction is expressed by the equation:



Alternatively, the titration may be conducted in the presence of alkali, the end-point being determined electrometrically.⁷

An iodometric method consists in estimating the iodine liberated from a mixture of potassium iodide and iodate,⁸ excess of which is added to the hydrosulphite solution, the reaction being according to the equation:



Excess of standard thiosulphate is added after the action and back-titrated with standard iodine.

Another method consists in titrating the hydrosulphite with iodine;

¹ Foerster, Lange, Drossbach and Seidel, *Zeitsch. anorg. Chem.*, 1923, 128, 278.

² Bosshard and Grob, *Chem. Zeit.*, 1913, 37, 423, 437; Helwig, *Amer. Dyestuff Reporter*, 1920, 7, ii., 12.

³ Seyewetz and Bloch, *Bull. Soc. chim.*, 1905, 38, 2051.

⁴ Orloff, *J. Russ. Phys. Chem. Soc.*, 1904, 36, 1311; also Bosshard and Grob, *loc. cit.* For a method of determination of each of the sulphur acids in a mixture containing sulphide, hydrosulphite, sulphite, thiosulphate and sulphate, see Binz and Sondag, *Ber.*, 1905, 38, 3830. For monographs on the hydrosulphites, see Jellinek, *Ahrens Sammlung*, 1911 and 1912.

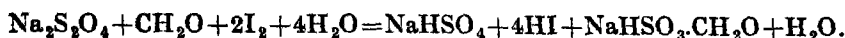
⁵ Smith, *J. Amer. Chem. Soc.*, 1921, 43, 1307.

⁶ Formhals, *Chem. Zeit.*, 1920, 44, 869; Bruhns, *Zeitsch. angew. Chem.*, 1920, 33, 92; Christiansen and Norton, *J. Ind. Eng. Chem.*, 1922, 14, 1126. See also Roth, *Zeitsch. angew. Chem.*, 1926, 39, 645.

⁷ del Fresno and Valdés, *Anal. Fis. Quim.*, 1929, 27, 368.

⁸ Wilkes, *J. Soc. Chem. Ind.*, 1923, 42, 356 T; Brotherton & Co., *ibid.*, *Chemistry and Industry Review*, 1923, 1, 1131.

in the presence of excess of formaldehyde the formaldehydesulphoxylate alone (see p. 228) reacts, thus : ¹



SULPHUR AND NITROGEN.²

Nitrogen forms at least three sulphides, nitrogen sulphide, N_4S_4 , nitrogen persulphide, NS_2 , and nitrogen pentasulphide, N_2S_5 , and it is possible that the sulphides of this element may prove as numerous as their oxygen analogues.

Nitrogen Sulphide or Sulphur Nitride, N_4S_4 .—Preparation.—Nitrogen sulphide may be prepared by the action of dry ammonia on "sulphur dichloride" dissolved in either carbon disulphide ³ or benzene : ⁴



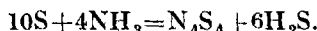
The ammonium chloride separates out in flakes, the solution becoming orange-red in colour. Since it is less soluble in carbon disulphide than sulphur, the nitrogen sulphide may be extracted from the product by fractional crystallisation from that solvent.

When ammonia and sulphur monochloride, S_2Cl_2 , each in ice-cold chloroform solution, are mixed, the main course of the reaction is :



After the sulphide N_4S_4 has been precipitated by the addition of alcohol, the mother-liquor on concentration yields nitrogen pentasulphide, N_2S_5 , and also hexasulphamide, S_6NH_2 .⁵

Sulphur reacts with liquid ammonia according to the equation :



The hydrogen sulphide may be removed as silver sulphide, whilst the nitrogen sulphide in the filtrate can be isolated by extraction with carbon disulphide.

Properties.—Nitrogen sulphide forms orange-coloured translucent monoclinic crystals with flat lustrous surfaces,⁶ $a : b : c = 0.8806 : 1 : 0.8430$; $\beta = 89^\circ 20'$. It has a density of 2.2, and melts at $179^\circ \text{C}.$,⁷ but the melting-point is considerably lowered by the presence of free sulphur. Sublimation occurs near the melting-point, and as the temperature rises the substance becomes highly explosive. It also detonates violently when struck. When heated in a vacuum, nitrogen sulphide sublimes without decomposition,⁸ but when sublimed in a vacuum over silver gauze at $360^\circ \text{C}.$, the sulphide is decomposed, the sulphur combining with the silver.⁹ Burt ¹⁰ noticed that, in addition to

¹ Merriman, *Chemistry and Industry Review*, 1923, 1, 290.

² See also Vol. VI., Part I., of this Series, Chapter XIII.

³ Souberran, *Ann. Chim. Phys.*, 1838, (2), 67, 71.

⁴ Schenck, *Annalen*, 1896, 290, 171.

⁵ Macbeth and Graham, *Proc. Roy. Irish Acad.*, 1923, 36, 31. See also Burt and Usher, *Proc. Roy. Soc.*, 1911, [A], 85, 82.

⁶ Artini, *Chem. Zentr.*, 1906, 1., 1774; Smith, *Min. Mag.*, 1911, 16, 97.

⁷ Vosnessenski, *J. Russ. Phys. Chem. Soc.*, 1927, 59, 221. See also Schenck, *loc. cit.*

⁸ Burt, *Trans. Chem. Soc.*, 1910, 97, 1171.

⁹ Burt and Usher, *Proc. Roy. Soc.*, 1911, [A], 85, 82.

¹⁰ Burt, *loc. cit.*

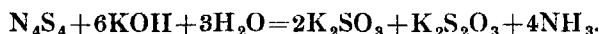
the evolution of nitrogen and the formation of silver sulphide due to the action of the silver gauze, a blue sulphide was also obtained having the same empirical formula as the yellow sulphide, thus furnishing an example of inorganic polymerism.¹

Nitrogen sulphide is only sparingly soluble in alcohol,² ether, wood spirit and turpentine; it is hydrolysed by water or moist air with formation of ammonium thiosulphate, ammonium trithionate and ammonia:



With hot water the reaction is violent.

With the alkalis the corresponding sulphite, thiosulphate and ammonia are formed:

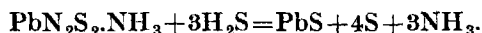


Dry ammonia has no action, but the sulphide dissolves in liquid anhydrous ammonia at -40°C ., yielding a red solution. After evaporation of the ammonia an orange or brown powder remains containing up to two molecules of ammonia, but this powder dissociates slowly even at ordinary temperatures.

Solutions of metallic iodides in anhydrous ammonia form precipitates with nitrogen sulphide in ammoniacal solution. Lead iodide thus forms the compound *lead dithiodi-imide*, $\text{PbN}_2\text{S}_2\cdot\text{NH}_3$, which crystallises in olive-green prisms, turning orange on exposure to the air. Hydrochloric acid reacts quantitatively with this lead compound according to the equation:

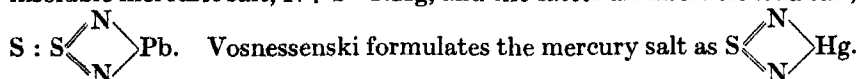


Dry liquid hydrogen sulphide reacts in accordance with the equation:

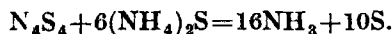


Although prepared in a similar manner to the lead compound, the product formed with mercury iodide contains one atom less of sulphur per molecule, thus, *mercury thiodi-imide*, $\text{HgN}_2\text{S}\cdot\text{NH}_3$.

Ruff and Geisel³ assume that the compound of nitrogen sulphide with ammonia dissociates in anhydrous ammonia solution forming (a), $\text{N} : \text{S} \cdot \text{NH}_2$, and (b), $\text{S} : \text{S}(\text{NH})_2$, of which the former yields an insoluble mercuric salt, $\text{N} : \text{S} \cdot \text{NHg}$, and the latter an insoluble lead salt,



Under similar conditions the cyanides of potassium, magnesium and aluminium form the corresponding *thiocyanates*. There are indications⁴ that the sulphur nitride reacts with ammonium sulphide in the solution to give sulphur, which then interacts with the cyanide:



¹ Usher, *Trans. Chem. Soc.*, 1925, 127, 130.

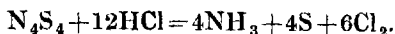
² For data of solubility in alcohol, carbon disulphide and benzene, see Vosnessenski, *loc. cit.*

³ Ruff and Geisel, *Ber.*, 1904, 37, 1573.

⁴ Bergstrom, *J. Amer. Chem. Soc.*, 1926, 48, 2319.

Silver and mercuric cyanides form thiocyanates, but considerable amounts of sulphides are also precipitated.

Heated to 120° C. in a closed platinum vessel, hydrogen fluoride and nitrogen sulphide unite to form a red liquid, which readily decomposes into its constituents. In the presence of traces of moisture, thionyl fluoride is formed. Dry hydrogen chloride reacts with nitrogen sulphide according to the equation : ¹



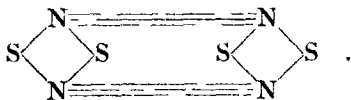
The sulphide, dissolved in benzene or alcohol, reacts with hydrogen sulphide forming ammonium polysulphide or ammonium thiosulphate, respectively.²

Many salts are capable of forming *additive products* with nitrogen sulphide, the components interacting in carbon tetrachloride solution. With *titanium tetrachloride*, TiCl_4 , a brownish-red amorphous compound is formed which reacts vigorously with water and with alkalis. According to Wölbling³ this substance has the composition $\text{N}_4\text{S}_4 \cdot \text{TiCl}_4$, but according to Davis⁴ the composition is $\text{N}_4\text{S}_4 \cdot \text{Ti}_2\text{Cl}_6$, reduction having taken place. *Antimony pentachloride* gives a stable scarlet compound, $\text{N}_4\text{S}_4 \cdot \text{SbCl}_5$. *Stannic chloride* yields an analogous red compound, $2\text{N}_4\text{S}_4 \cdot \text{SnCl}_4$. *Stannous chloride* does not combine directly with nitrogen sulphide, but in warm benzene solution a yellow compound is obtained, the constitution of which has not been determined. With *selenium dichloride* a green compound, $\text{N}_4\text{S}_4 \cdot \text{SeCl}_2$, is obtained. In the case of *tungsten hexachloride* the compound formed is $\text{N}_4\text{S}_4 \cdot \text{WCl}_6$, reduction having taken place.⁵

The addition of "*sulphur dichloride*" to nitrogen sulphide in solution also yields *additive products*, the following having been prepared : ⁶ $3\text{N}_4\text{S}_4 \cdot 2\text{SCl}_2$, $\text{N}_4\text{S}_4 \cdot \text{SCl}_2$ and $\text{N}_4\text{S}_4 \cdot 2\text{SCl}_2$.

Nitrogen sulphide acts slowly on the acids of the paraffin series. In the case of acetic acid there is an evolution of sulphur dioxide, and sulphur and ammonium sulphate are obtained, as well as small quantities of free nitrogen. Considerable quantities of acetamide and diacetamide are also formed.⁷ The sulphide is indifferent towards primary and secondary bases of the aromatic series and towards all tertiary bases.⁸ Nitrogen sulphide has been claimed to assist the vulcanisation of rubber.

Constitution.—According to Schenck,⁹ and Clever and Muthmann,¹⁰ nitrogen sulphide has the constitution



¹ Ruff and Geisel, *Ber.*, 1904, 37, 1573.

² Wölbling, *Zeitsch. anorg. Chem.*, 1908, 57, 281.

³ Wölbling, *loc. cit.*

⁴ Davis, *Trans. Chem. Soc.*, 1906, 89, 1576.

⁵ Davis, *loc. cit.*

⁶ Vosnessenski, *J. Russ. Phys. Chem. Soc.*, 1927, 59, 221

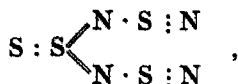
⁷ Francis, *Trans. Chem. Soc.*, 1905, 87, 1836.

⁸ Schenck, *Annalen*, 1896, 290, 171. For certain colour reactions of N_4S_4 , see Vosnessenski, *J. Russ. Phys. Chem. Soc.*, 1928, 60, 1037.

⁹ Schenck, *loc. cit.*

¹⁰ Clever and Muthmann, *Ber.*, 1896, 29, 340.

Ruff and Geisel¹ consider that its most probable constitution is



their researches on the sulphur halides rendering the bivalency of all the sulphur atoms in the sulphide improbable.²

The latter formula is in accordance with the behaviour of the sulphide on hydrolysis, its reaction with hydrogen chloride, and with the formula-

tion of the metallic derivatives $\text{S} : \text{S} \begin{array}{l} \nearrow \text{N} \\ \searrow \text{N} \end{array} \text{Pb}$ and $\text{S} : \text{S} \begin{array}{l} \nearrow \text{N} \\ \searrow \text{N} \end{array} \text{Hg}$. The

action of acetyl chloride, which produces the compound $\text{N}_3\text{S}_4\text{Cl}$ (p. 238), and the recovery of nitrogen sulphide from this compound by the action of ammonia, are facts which cannot be explained by this for-

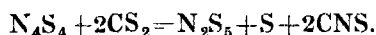
mula,³ nor does the cyclic formula, $\text{N} \begin{array}{c} \text{S}=\text{N}-\text{S} \\ | \quad | \\ \text{S}-\text{N}=\text{S} \end{array} \text{N}$, put forward by

Meuwsen,⁴ completely satisfy. The constitution is not, therefore, completely elucidated.

Nitrogen Persulphide, NS_2 .—When nitrogen sulphide, N_4S_4 , is sublimed with sulphur at 125°C . (in the absence of silver gauze, cf. p. 233), nitrogen persulphide is obtained as a dark-red liquid, somewhat resembling bromine, which, at the temperature of solid carbon dioxide, solidifies to a pale yellow solid. The liquid has a penetrating odour resembling that of iodine, and can be distilled unchanged in a vacuum. At ordinary temperatures it decomposes slowly, forming yellow nitrogen sulphide and sulphur. The persulphide is decomposed by water into free sulphur, and ammonium salts are formed.⁵

Nitrogen Pentasulphide, N_2S_5 .—Nitrogen pentasulphide is formed by the decomposition of the yellow sulphide, N_4S_4 , and its derivatives. It is formed, for example, when the yellow sulphide is exploded by friction, when the compounds of N_4S_4 with the halogens or with nitrous or nitric acid are boiled with water, and also when N_4S_4 is heated carefully with lead oxide.⁶

The pentasulphide may be prepared by heating together yellow nitrogen sulphide and carbon disulphide under pressure :



A deep red solution is obtained and a brown precipitate. The solution consists of nitrogen pentasulphide and sulphur in carbon disulphide, the pentasulphide being extracted by means of ether. If the product is pure, containing no sulphur, it crystallises from the ether solution in tablets of metallic appearance somewhat resembling iodine. The brown precipitate has the composition $\text{C}_3\text{N}_3\text{S}_3$ (see p. 281).

Nitrogen pentasulphide may also be obtained by the action of carbon

¹ Ruff and Geisel, *Ber.*, 1904, 37, 1573.

² Ruff and Fischer, *ibid.*, 1903, 36, 418; Ruff and Winterfeld, *ibid.*, p. 2437.

³ Vosnessenski, *J. Russ. Phys. Chem. Soc.*, 1927, 59, 221.

⁴ Meuwsen, *Ber.*, 1929, 62, [B], 1959.

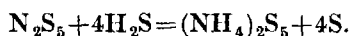
⁵ Usher, *Trans. Chem. Soc.*, 1926, 127, 730. Moldenhauer (*Ber.*, 1929, 62, [B], 2390) describes a bluish-black disulphide, $(\text{NS}_2)_x$.

⁶ Muthmann and Clover, *Zeitsch. anorg. Chem.*, 1896, 13, 200.

tetrachloride on N_4S_4 at $125^\circ C$. In this case a black complex by-product is obtained.

The action of zinc dust on a suspension of thiotriithiazyl chloride, N_3S_3Cl (see p. 288), also gives the pentasulphide.

Nitrogen pentasulphide is a deep red liquid, which solidifies to a crystalline mass strongly resembling iodine. It melts at 10° to $11^\circ C$. Its specific gravity at $18^\circ C$. is 1.901. It is insoluble in water but soluble in most organic solvents. It is unstable in solution, especially on exposure to light, the products of its decomposition being N_4S_4 and sulphur. When boiled with water or with aqueous solutions of the caustic alkalis, ammonia and sulphur are formed. An alcoholic solution of an alkali hydroxide added to an alcoholic solution of nitrogen pentasulphide produces a transient but intense violet-red coloration. So characteristic is this reaction that it may be used for the detection of very small quantities of the pentasulphide. Alcoholic solutions of the alkali sulphides yield ammonia and a polysulphide. With hydrogen sulphide, ammonium polysulphide and sulphur are formed, thus :



The pentasulphide is violently oxidised by concentrated nitric acid, with formation of sulphuric acid, whilst dilute hydrochloric or sulphuric acid yields the ammonium salt and sulphur.

Cryoscopic determinations of the molecular weight, using benzene as solvent, give results agreeing with the formula N_2S_5 .

Sulphammonium, $S(NH_3)_x$.—When sulphur reacts with liquid ammonia at temperatures varying between $-38^\circ C$. and $-11.5^\circ C$., the solution obtained is blue in colour and from it red, fern-like leaflets are obtainable, to which the name sulphammonium has been given.¹ Sulphammonium is formed also by the action of hydrogen sulphide on nitrogen sulphide, N_4S_4 , dissolved in ammonia at $-35^\circ C$., and by the action of ammonia and a limited amount of hydrogen sulphide on lead or mercury dithiodi-imide.² Red, fern-like leaflets of solid sulphammonium are also produced by submitting a mixture of nitrogen and ammonia at $-12^\circ C$. to a pressure of 45 atmospheres in the presence of sulphur.

Examination of the absorption of light of various wave-lengths by solutions of hydrogen sulphide and nitrogen sulphide in liquid ammonia shows that several compounds must exist.

Sulphammonium decomposes into ammonia and sulphur under ordinary pressures. With liquid ammonia in sealed tubes at temperatures between $0^\circ C$. and $20^\circ C$. it gives the compound $(NH_3)_2S.2NH_3$, and at $-28^\circ C$. it forms $(NH_3)_2S.NH_3$. With iodine in solution in liquid ammonia, sulphammonium forms an ammoniacal compound of sulphur iodide. The blue colour of a solution of sulphammonium may possibly be due to the presence of colloidal sulphur.³

Hexasulphamide, S_6NH_2 .—In the preparation of nitrogen sulphide, N_4S_4 , from ammonia and sulphur monochloride, as already described (p. 283), the mother-liquor may, on concentration, yield hexasulphamide in addition to nitrogen pentasulphide. Hexasulphamide crystallises in colourless, square plates, melting at $105^\circ C$. It is insoluble in water

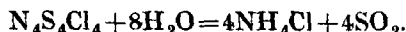
¹ Moissan, *Compt. rend.*, 1901, 132, 510.

² Ruff and Geisel, *Ber.*, 1905, 38, 2859.

³ See also Ruff and Hecht, *Zeitsch. anorg. Chem.*, 1911, 70, 49.

but soluble in most organic solvents. It gives a coloration with alcoholic potash and with alcoholic solutions of organic bases.¹

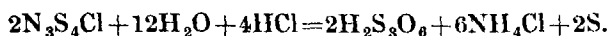
Nitrogen Chlorosulphide, $N_4S_4Cl_4$.—This is obtained by the action of chlorine on nitrogen sulphide, N_4S_4 , either in chloroform solution or suspended in carbon tetrachloride.² The chlorosulphide is a yellow, crystalline solid, unstable in moist air; it is also unstable when kept under carbon tetrachloride, but crystallises from hot dry benzene without decomposition. It decomposes on heating with formation of some sulphur monochloride and nitrogen. The sulphur chloride formed may reunite with part of the chlorosulphide to form the stable compound, trithiazyl chloride, N_3S_3Cl . This change takes place rapidly at $100^\circ C$. Water decomposes nitrogen chlorosulphide according to the equation:



The chlorosulphide is reconverted into nitrogen sulphide by the action of cold ammonia. When treated with dry hydrogen chloride in benzene solution it yields a bright yellow compound which is only slightly decomposed by cold water but immediately by lukewarm water.

Trithiazyl Chloride, N_3S_3Cl , is formed by the decomposition of nitrogen chlorosulphide. It forms stable copper-coloured needles, which are slightly soluble in chloroform.³

Thiotrithiazyl Chloride, N_3S_4Cl , is obtained when nitrogen sulphide, N_4S_4 , is added to "sulphur dichloride" dissolved in its own volume of chloroform or carbon tetrachloride and the resulting mixture boiled.⁴ It is more conveniently prepared by heating nitrogen sulphide with acetyl chloride.⁵ Thiotrithiazyl chloride is a yellow, crystalline solid, insoluble in most solvents but slightly soluble in thionyl chloride, from which it crystallises in brownish crystals. It is decomposed by water, forming ammonium trithionate, ammonium chloride and sulphur. Similarly it yields trithionic acid with dilute hydrochloric acid: ⁶



With concentrated nitric acid, thiotrithiazyl chloride yields *thiotrithiazyl nitrate*, $N_3S_4NO_3$.⁷ Like nitrogen sulphide, with dilute aqueous alkali it yields sulphite and thiosulphate.⁸ When thiotrithiazyl chloride is boiled with alcohol and the resulting solution treated with a few drops of alcoholic potash, an intense violet-red coloration is produced. Ammonia gas is rapidly absorbed by the dry compound, which then explodes violently after a few minutes. If thiotrithiazyl chloride is suspended in chloroform and submitted to the action of a stream of ammonia gas, the liquid becomes orange-red; ammonium chloride and ammonium sulphide are produced and nitrogen sulphide is regenerated.⁹

Dithiotetrathiazyl Chloride, $N_4S_6Cl_2$, may be prepared by the

¹ Macbeth and Graham, *Proc. Roy. Irish Acad.*, 1923, 36, 31.

² Demarçay, *Compt. rend.*, 1880, 91, 854; 1881, 92, 726; Androocci, *Zeitsch. anorg. Chem.*, 1897, 14, 246.

³ Demarçay, *loc. cit.*

⁴ Wölbling, *Zeitsch. anorg. Chem.*, 1908, 57, 281.

⁵ Muthmann and Seitter, *Ber.*, 1897, 30, 627.

⁶ Vosnessenski, *J. Russ. Phys. Chem. Soc.*, 1928, 60, 1037.

⁷ Demarçay, *Compt. rend.*, 1881, 91, 1066.

⁸ Vosnessenski, *loc. cit.*

⁹ Muthmann and Seitter, *loc. cit.*

action of nitrogen sulphide, N_4S_4 , on sulphur monochloride in the cold. It is deposited as a black, crystalline solid, which on heating decomposes thus :



Crystals of dithiotetrathiazyl chloride make a crimson mark on paper.¹

By the action of nitrogen sulphide, N_4S_4 , on a chloroform solution of nitrogen chlorosulphide, $N_4S_4Cl_4$, a copper-coloured compound is obtained, possibly of composition N_3S_3Cl . This compound is less soluble in chloroform than nitrogen chlorosulphide and does not change so readily. It decomposes with a feeble explosion when strongly heated.¹

Nitrogen sulphide, N_4S_4 , forms various compounds with "sulphur dichloride" when the two are mixed in carbon disulphide solution² (see p. 235). In the presence of excess of "sulphur dichloride" the product is **thiodithiazyl dichloride**, $N_2S_3Cl_2$ or $N_4S_4 \cdot 2SCl_2$. This compound has also been prepared by the union of "sulphur dichloride" with thiotrithiazyl chloride.³ Thiodithiazyl dichloride forms yellow crystals which decompose in air, losing a part of their sulphur chloride and becoming reddish-black in colour. With concentrated sulphuric acid, hydrogen chloride is liberated and a red solution is formed. Water acts on the dichloride with formation of a black compound of composition $N_2S_3O_3$. Chlorine reacts with formation of nitrogen chlorosulphide, $N_4S_4Cl_4$. At 100° C. thiodithiazyl dichloride decomposes with evolution of chlorine and nitrogen chlorosulphide. The residue consists of thiotrithiazyl chloride.

A red compound of composition $N_4S_4 \cdot SCl_2$ is also obtained by the interaction of "sulphur dichloride" and nitrogen sulphide in carbon disulphide solution, and consequently it is formed during the preparation of nitrogen sulphide by the action of ammonia on the dichloride in carbon disulphide (p. 233). It decomposes at 100° C., forming the compound $3N_4S_4 \cdot 2SCl_2$, which substance is also obtained when excess of nitrogen sulphide is added to "sulphur dichloride." $3N_4S_4 \cdot 2SCl_2$ is a yellow powder, which is slightly soluble in carbon disulphide and yields a blue substance with water. A fleeting violet coloration is produced by the action of alcoholic potash.⁴

Nitrogen Bromosulphide, $N_4S_4Br_4$.—When nitrogen sulphide is treated with bromine in carbon disulphide solution, bronze-coloured crystals of nitrogen bromosulphide are obtained. This compound decomposes in moist air, forming a yellow, amorphous compound, of composition $N_4S_5Br_2$, perhaps $N_4S_4 \cdot SBr_2$. Nitrogen sulphide also absorbs bromine vapour, forming red crystals having the composition $N_4S_4Br_4$. This latter is a very unstable compound; carbon disulphide deprives it of some bromine, and it decomposes in moist air with formation of the yellow compound $N_4S_5Br_2$. With nitrogen peroxide in carbon disulphide solution it yields crystals of a compound NSO_4 , which is decomposed by water into nitric oxide and sulphuric acid. If nitrogen bromosulphide, $N_4S_4Br_4$, is digested with nitrogen peroxide in carbon

¹ Demarçay, *loc. cit.*

² Fordos and Gélis, *Ann. Chim. Phys.*, 1851, (3), 32, 403.

³ Demarçay, *Compt. rend.*, 1880, 91, 854, 1066; 1881, 92, 726.

⁴ Demarçay, *loc. cit.*

disulphide solution, yellow crystals are formed, apparently of composition NSO, but very unstable, gentle heat causing complete decomposition. Similar treatment with nitrogen peroxide converts the compound $N_4S_4Br_2$ into $N_4S_4O_8$, which yields large yellow crystals.¹

Thiotrithiazyl Bromide, N_3S_4Br , is obtained by the interaction of nitrogen sulphide, N_4S_4 , and "sulphur dibromide," SBr_2 , in chloroform solution. In carbon disulphide solution the product obtained has the composition N_4S_5Br .² Thiotrithiazyl bromide is also formed when excess of bromine acts on thiotrithiazyl chloride in warm carbon disulphide solution. It is also produced when nitrogen bromosulphide, $N_4S_4Br_4$, is exposed to the action of moist air.³ Thiotrithiazyl bromide forms small, yellow, needle-shaped crystals, stable in air. On boiling with water the products are ammonium bromide, sulphur and sulphur dioxide. Hot dilute alkalis yield ammonia, together with the alkali bromide, thiosulphate and sulphide.

Thiotrithiazyl Iodide, N_3S_4I , may be prepared by dissolving thiotrithiazyl chloride in ice-cold water and adding excess of an ice-cold solution of potassium iodide. It is also formed by the action of iodine dissolved in methyl alcohol on thiotrithiazyl chloride, but prepared in this way it is invariably contaminated with chlorine. It is a dark red crystalline powder which decomposes spontaneously with evolution of iodine on exposure to air.³

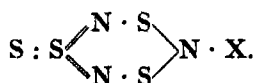
Thiotrithiazyl Nitrate, $N_3S_4NO_3$, may be obtained by dissolving thiotrithiazyl chloride in concentrated nitric acid and evaporating the yellow liquid produced in a vacuum. It forms long, yellow, transparent, prismatic crystals, which become opaque after several days and acquire the odour of sulphur dioxide and the oxides of nitrogen. It is explosive. Its solution in water is yellow at first, but quickly becomes opaque, depositing a black substance mixed with a large amount of sulphur.³

Nitrosulphonic Anhydride, $N_2S_2O_9$.—For this substance see p. 250.

Thiotrithiazyl Hydrogen Sulphate, $N_3S_4.HSO_4$, is obtained when thiotrithiazyl chloride is dissolved in concentrated sulphuric acid. There is an evolution of hydrogen chloride and, on addition of acetic acid to the solution, the hydrogen sulphate is deposited as pale yellow needles.⁴

Thiotrithiazyl Thiocyanate, N_3S_4CNS , is obtained by adding a solution of potassium thiocyanate to an ice-cold solution of thiotrithiazyl chloride or nitrate. It forms lustrous bronze leaflets, readily soluble in benzene and chloroform.

Muthmann and Seitter³ regard these thiotrithiazyl compounds as having the constitutional formula



¹ Clever and Muthmann, *Ber.*, 1896, 29, 340.

² Wöhlung, *Zeitsch. anorg. Chem.*, 1908, 57, 281.

³ Muthmann and Seitter, *Ber.*, 1897, 30, 627.

⁴ Demarçay, *Compt. rend.*, 1880, 91, 854, 1066.

Amides of the Sulphur Oxy-acids.

These compounds stand in close relationship with the corresponding acid chlorides, which have been described earlier.

Thionylamide, $\text{SO}(\text{NH}_2)_2$, the amide of sulphurous acid, is unknown, although indications of the existence of an unstable *imido-sulphinamide*, $\text{NH}(\text{SO}.\text{NH}_2)_2$, have been observed in the product of the interaction of thionyl chloride and liquid ammonia.

Sulphamide, $\text{SO}_2(\text{NH}_2)_2$, the amide of sulphuric acid, may be obtained by the action of dry ammonia upon a cooled solution of sulphuryl chloride in either ethylene chloride or chloroform solution: ¹



It is better prepared by saturating a solution of sulphuryl chloride in 15 to 20 times its volume of chloroform with ammonia and shaking the product with water until the precipitate has dissolved. The aqueous solution, after boiling with lead oxide or silver oxide to remove chlorine and filtering, yields a viscid, hygroscopic liquid on evaporation.²

Another method of preparation for pure sulphamide is to dissolve the product of the reaction between sulphuryl chloride and liquid ammonia in a small quantity of water and acidify the solution in order to cause hydrolysis. After two or three days, when hydrolysis is complete, the mixture is evaporated to dryness *in vacuo* and the residue extracted with ethyl acetate. The sulphamide is dissolved out and on evaporating off the ethyl acetate, pure sulphamide is obtained.³

Sulphamide forms large, colourless, tabular crystals, which melt between 91.5° and 93° C. It is tasteless, only sparingly soluble in water or dilute alcohol, and neutral in reaction. On heating to 100° C. it begins to lose ammonia, with formation of *imidodisulphamide*, $\text{NH}_2.\text{SO}_2.\text{NH}.\text{SO}_2.\text{NH}_2$, and at 250° C. it decomposes completely, with loss of sulphur dioxide. With ammoniacal silver nitrate a precipitate is produced, which on heating to a temperature of 170° to 180° C. (preferably with a little ammonium chloride) until evolution of ammonia ceases, deposits the silver salt of sulphamide, SO_2NAg . On heating, this compound yields metallic silver mixed with a little silver sulphate. Sulphamide dissolves readily in cold concentrated nitric acid without nitration. On the addition of concentrated sulphuric acid, *nitro-sulphamide*, $\text{NH}_2.\text{SO}_2.\text{NH}.\text{NO}_2$, is precipitated. This, on reduction with zinc dust and dilute sulphuric acid, yields first, hydrazine sulphonamide, $\text{NH}_2.\text{SO}_2.\text{NH}.\text{NH}_2$, and ultimately, amidosulphonic acid and hydrazine sulphonamic acid or their zinc salts.

Sulphamide absorbs

1.4	molecular proportions of dry ammonia at $+20^\circ$ C.
3.0	" " " " " 0° C.
5.4	" " " " " -20° C.

In the pure state, sulphamide is a non-electrolyte, indicating the weakness of its acidic tendencies. With the alkalis it forms salts, but not more than two atoms of hydrogen are displaceable by the metal.⁴

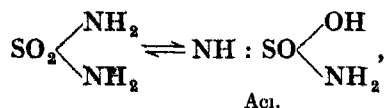
¹ Regnault, *Ann. Chim. Phys.*, 1838, 69, 170.

² Ephraïm and Gurewitsch, *Ber.*, 1910, 43, 138.

⁴ Hantzsch and Holl, *ibid.*, 1901, 34, 3430.

³ Traube, *Ber.*, 1892, 25, 2472.

From a consideration of the electrical conductivities of its solutions it has been suggested ¹ that sulphamide may also exist in an *aci* form, thus :



just as in the case of carbamide.

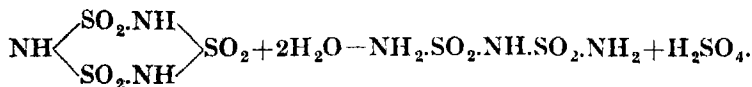
Imidodisulphamide, $\text{NH}_2 \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{SO}_2 \cdot \text{NH}_2$, is the first product of the action of ammonium carbamate on pyrosulphuryl chloride.² It is also obtained when sulphamide is heated nearly to its melting-point. Imidodisulphamide forms needle-shaped colourless crystals, melting at 160° C., and having a distinctly acid taste, since water causes rapid decomposition into sulphamide and amidosulphonic acid :



Sulphimide, or **Trisulphimide**, $(\text{SO}_2\text{NH})_3$.—This is formed together with ammonia and imidosulphonic acid when sulphamide is heated at 200° to 210° C. It is also formed in small quantity as the ammonium salt, together with sulphamide, when sulphuryl chloride is treated with ammonia in chloroform solution : ⁴



Sulphimide is described ⁵ as consisting of glistening white needles, melting at about 165° C., readily soluble in water, alcohol and acetone, sparingly soluble in ether and insoluble in benzene or chloroform. It is decomposed by hydrogen chloride with formation of ammonia and sulphuric acid. Ebullioscopic determinations of the molecular weight in ethyl acetate solution point to the formula $(\text{SO}_2\text{NH})_3$. Hantzsch and Stuer, however,⁶ are of opinion that trisulphimide is unknown in the solid form, and that the substance previously described as sulphimide is really imidodisulphamide, $\text{NH}_2 \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{SO}_2 \cdot \text{NH}_2$, produced by the action of water on trisulphimide :



The Sulphonic Acids.

Just as chlorosulphonic acid may be regarded as derived from hydrochloric acid by the substitution of the group $-\text{SO}_2\text{OH}$ in place of the hydrogen atom, so also many other compounds are known which likewise may be considered as produced by the introduction of the sulphonic acid group in place of hydrogen.

For example, ammonia and its hydroxy derivatives yield a series of sulphonic acids, their relationships being represented by the following table : ⁷

¹ Traube and Reubke, *Ber.*, 1923, 56, [B], 1656.

² Mente, *Annalen*, 1888, 248, 232.

³ Hantzsch and Holl, *Ber.*, 1901, 34, 3430; Hantzsch and Stuer, *ibid.*, 1905, 38, 1022.

⁴ Traube, *ibid.*, 1893, 26, 207.

⁵ Hantzsch and Holl, *loc. cit.*

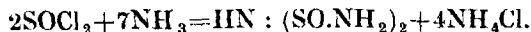
⁶ Hantzsch and Stuer, *Ber.*, 1905, 38, 1022.

⁷ Raschig, *Annalen*, 1887, 241, 161; Frémy, *Ann. Chim. Phys.*, 1845, (3), 15, 408; Claus and Koch, *Zeitsch. Chem. Phys. Math.*, 1861, (2), 4, 684; *Ber.*, 1871, 4, 186, 221, 504.

NH_3 , Ammonia.	HO.NH_2 , Hydroxylamine.	NH(OH)_2 , Dihydroxyammonia.	N(OH)_2 , "Ortho-nitrous" acid
$\text{NH}_2.\text{SO}_2.\text{OH}$, Amidosulphonic acid.	$\text{HO.NH.SO}_2.\text{OH}$, Hydroxylamine-sulphonic acid.	$\text{OH.SO}_2.\text{N(OH)}_2$, Dihydroxylamine-sulphonic acid	
$\text{NH(SO}_2.\text{OH)}_2$, Imidosulphonic acid.	$\text{HO.N(SO}_2.\text{OH)}_2$, Hydroxylamine-disulphonic acid.		
$\text{N(SO}_2.\text{OH)}_2$, Nitrilosulphonic acid.			

The foregoing sulphonic acids are all known, at least in the form of their salts, and are obtainable, directly or indirectly, by the interaction of sulphurous and nitrous acids or their salts. Isomerides of some of the sulphonic acids are also known, for example, hydroxylamine-*iso*-sulphonic acid, $\text{NH}_2.\text{O.SO}_2.\text{OH}$,¹ which is obtainable by the action of chlorosulphonic acid on hydroxylamine hydrochloride. As its constitution indicates, this isomeric acid is in reality a derivative of permonosulphuric acid (see p. 192).

By the action of sulphur dioxide on ammonia three different compounds may be formed, the product depending on the conditions of the reaction. The proportions in which the gases combine depend largely on the extent to which the temperature is allowed to rise, the heat of union being considerable. The product also varies according to which gas is present in excess, unless the temperature is kept very low, in which case ammonium amidosulphinate is formed. When sulphur dioxide is in excess the yellow, crystalline *amidosulphinic acid*, $\text{NH}_3.\text{SO}_2$ or $\text{NH}_2.\text{SO}_2\text{H}$, is formed. With excess of ammonia the product may be either the white, crystalline salt, *ammonium amidosulphinate*, $2\text{NH}_3.\text{SO}_2$ or $\text{NH}_2.\text{SO}_2.\text{NH}_4$, or *triammonium imidodisulphinate*, $4\text{NH}_3.2\text{SO}_2$ or $\text{NH}_4.\text{N} : (\text{SO}_2.\text{NH}_4)_2$, a red compound, having the same percentage composition as ammonium amidosulphinate but of double molecular weight. That in the molecule of this latter substance three of the nitrogen atoms are placed differently from the fourth is evident from the formation of a silver salt, $\text{Ag.N} : (\text{SO}_2\text{Ag})_2$, which is also red in colour. Triammonium imidodisulphinate is also obtainable by the action of thionyl chloride on liquid ammonia, a diamide first being formed:



The diamide is hydrolysed by water to $\text{NH(SO}_2.\text{NH}_4)_2$, which reacts with more ammonia to form the triammonium salt. On evaporation, and digestion of the residue with absolute alcohol at -5°C ., a red solution is obtained, which, when evaporated in a vacuum, yields the triammonium salt in the form of red flakes.²

¹ Sommer and Templin, *Ber.*, 1914, 47, 1221. See also Raschig, *ibid.*, 1906, 39, 245; Haga, *Trans. Chem. Soc.*, 1906, 89, 240.

² For detailed accounts of these products, see Divers, *Trans. Chem. Soc.*, 1900, 77, 440, 432; 1901, 79, 1093; Divers and Ogawa, *ibid.*, 1901, 79, 1102; Ephraim and Piotrowski, *Ber.*, 1911, 44, 379; also Schumann, *Zeitsch. anorg. Chem.*, 1900, 23, 43.

Ammonia combines with sulphur trioxide to form at least six different compounds : ¹

$\text{NH}_3 \cdot 2\text{SO}_3$ or $\text{HN}(\text{SO}_3\text{H})_2$, Imidosulphonic acid.

$\text{NH}_3 \cdot \text{SO}_3$ or $\text{H}_2\text{N} \cdot \text{SO}_3\text{H}$, Amidosulphonic acid.

$4\text{NH}_3 \cdot 3\text{SO}_3$ or $\text{N}(\text{SO}_3\text{NH}_4)_3$, Ammonium nitrilosulphonate.

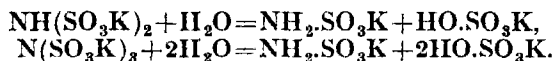
$3\text{NH}_3 \cdot 2\text{SO}_3$ or $\text{HN}(\text{SO}_3\text{NH}_4)_2$, Diammonium imidosulphonate (para-sulphat-ammon).

$4\text{NH}_3 \cdot 2\text{SO}_3$ or $(\text{NH}_4)\text{N}(\text{SO}_3\text{NH}_4)_2$, Normal ammonium imidosulphonate (sulphat-ammon).

$2\text{NH}_3 \cdot \text{SO}_3$ or $\text{H}_2\text{N} \cdot \text{SO}_3 \cdot \text{NH}_4$, Ammonium amidosulphonate.

These six compounds can all be derived the one from the other, with the exception of the nitrilosulphonate, which cannot be re-formed from the others although it is itself the most convenient source of them. Nitrilosulphonic acid would, if it existed in the free state, be the seventh of these compounds, heading the column as $\text{NH}_3 \cdot 3\text{SO}_3$ or $\text{N}(\text{SO}_3\text{H})_3$.

Amidosulphonic Acid, $\text{NH}_2 \cdot \text{SO}_3\text{H}$, may be obtained by the action of sulphur trioxide on dry ammonia.² When an aqueous solution of hydroxylamine hydrochloride is saturated with sulphur dioxide and afterwards evaporated, amidosulphonic acid is obtained.³ Potassium imidosulphonate, $\text{NH}(\text{SO}_3\text{K})_2$, and potassium nitrilosulphonate, $\text{N}(\text{SO}_3\text{K})_3$, are both decomposed by hot water with formation of potassium amidosulphonate : ⁴



Amidosulphonic acid may also be prepared ⁵ by passing sulphur dioxide into an aqueous solution of sodium nitrite containing sodium carbonate, until the solution is acid to litmus; the nitrilosulphonate which is formed is hydrolysed by the addition of a little concentrated sulphuric acid, amidosulphonate and acid sulphate being formed. The solution is neutralised by the addition of sodium carbonate and the sodium sulphate formed separated by crystallisation; the addition of a large excess of concentrated sulphuric acid to the solution then results in the precipitation of amidosulphonic acid.

Amidosulphonic acid is a colourless, odourless, crystalline solid, specific gravity 2.03 at 12° C. It decomposes to a large extent during melting but has an apparent melting-point of 205° C. It is slowly soluble in water, requiring five parts of water at 0° C. and half this amount at 70° C. to dissolve it. It is stable in air and not deliquescent. Although it is not precipitated by solutions of barium chloride it retards the precipitation of small quantities of sulphuric acid by barium chloride. It forms a compound with oxide or nitrate of mercury, which is insoluble in dilute nitric acid and probably has the composition $\text{Hg}_3\text{N}_2(\text{SO}_3\text{H})_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. When amidosulphonic acid, or any of its salts, is heated, partial conversion into imidosulphonate and ammonia occurs,



¹ Divers and Haga, *Trans. Chem. Soc.*, 1901, 79, 1095; 1892, 61, 945.

² Rose, *Ann. Phys. Chem.*, 1834, 33, 235.

³ Raschig, *Ber.*, 1887, 20, 584.

⁴ See also Berglund, *Ber.*, 1876, 9, 1896.

⁵ Divers and Haga, *Trans. Chem. Soc.*, 1896, 69, 1039.

and partial conversion into sulphate and gaseous products. Thus, in the case of the barium salt, the decomposition may be represented by the equation :¹



The potassium salt reacts in the cold with an equivalent amount of hypochlorous acid to form *potassium chloramidosulphonate*, $\text{NHCl}\cdot\text{SO}_3\text{K}$, which may be isolated by evaporation to small bulk *in vacuo* and precipitation with alcohol.² It is a comparatively stable, hygroscopic, crystalline salt, hydrolysed by mineral acids to form ammonium chloride and sulphuric acid. The corresponding bromine compound is similar in properties. Barium forms a less stable chloro-compound.

Amidosulphonic acid reacts quantitatively with the alkalis, and with carbonates and borates, and its use as a primary standard in volumetric analysis has been suggested.³

Imidosulphonic Acid, $\text{NH}(\text{SO}_3\text{H})_2$, the amide of which has already been described (p. 242), may be obtained as the ammonium salt by mixing sulphuric anhydride vapour with excess of gaseous ammonia and fusing the condensed flocculent product in an atmosphere of ammonia :



The potassium salt may be obtained by heating potassium nitrilosulphonate with water :

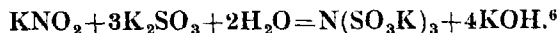


The lead salt, on decomposition with hydrogen sulphide, yields the free acid.

The salts of this acid may either be neutral, of the type $\text{NH}(\text{SO}_3\text{R})_2$, or "basic," corresponding to $\text{NR}(\text{SO}_3\text{R})_2$. The basic salts are more soluble in water than the neutral salts.

Imidosulphonic acid is decomposed by dilute hydrochloric acid, forming amidosulphonic acid and sulphuric acid.

Nitrilosulphonic Acid, $\text{N}(\text{SO}_3\text{H})_3$, has long been known in the form of its potassium salt, which is precipitated in crystalline condition when a mixture of potassium nitrite and potassium sulphite (1 mol. : 3 mols.) is allowed to stand :



The nitrilosulphonates can only be prepared by the sulphonation of hydroximidosulphonates, which process resolves itself into treating the corresponding nitrite in this way, since the hydroximidosulphonate has itself to be prepared by a similar sulphonation of the nitrite.⁷

Hydroxylamine-monosulphonic Acid, $\text{NH}(\text{OH})\cdot\text{SO}_3\text{H}$.—This

¹ Divers and Haga, *Trans. Chem. Soc.*, 1896, 69, 1634. For the physiological action of amidosulphonic acid, see Loew, *ibid.*, p. 1662; *Chem. News*, 1896, 74, 277.

² Traube and von Drathen, *Ber.*, 1918, 51, 111.

³ Misutsch, *Pharm. J. (Russia)*, 1928, p. 310; *Chem. Zentr.*, 1928, n., 1129.

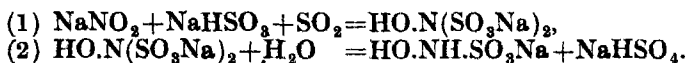
⁴ Rose, *Ann. Phys. Chem.*, 1834, 33, 235; Jacquelin, *Ann. Chim. Phys.*, 1843, (3), 8, 293; Woronin, *Jahresber.*, 1859, 3, 273.

⁵ Claus and Koch, *Annalen*, 1869, 152, 335, 351.

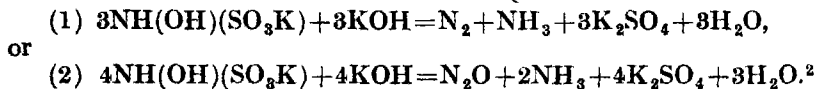
⁶ Claus, *ibid.*, p. 336; 1871, 158, 52, 194; Frémy, *Ann. Chim. Phys.*, 1845, [3], 15, 408; Berglund, *Ber.*, 1876, 9, 252.

⁷ Divers and Haga, *Trans. Chem. Soc.*, 1901, 79, 1093.

compound has been very completely studied by Raschig.¹ The sodium salt is formed according to the following reactions :



The free acid is very stable. Hot alkalis decompose it according to the equations :



Nitrososulphonic Acid or Nitrosohydroxylamine-sulphonic Acid, $\text{N}(\text{NO})(\text{OH})\text{SO}_3\text{H}$ or $\text{HO}_2\text{N}_2\text{SO}_3\text{H}$.—The sodium salt of this acid has been prepared by the action of nitric oxide on a caustic soda solution of sodium sulphite :³



The alkali nitrososulphonates are decomposed by acids with formation of nitrous oxide and the corresponding sulphate. With barium chloride the nitrososulphonates yield a white precipitate which is soluble in hydrochloric acid.⁴

Hydroxylamine-disulphonic Acid, $\text{N}(\text{OH})(\text{SO}_3\text{H})_2$.—The alkali hydroxylamine-disulphonates may be prepared by the addition of the alkali hydrogen sulphite in concentrated aqueous solution to the alkali nitrite. They are also formed when excess of sulphur dioxide is passed through a solution containing the alkali nitrite and either the alkali carbonate or hydroxide. The presence of caustic alkali confers stability on the compound, whilst acids decompose it even in the cold, hydroxylamine monosulphonic acid being formed.⁵

Hydroxylamine-isodisulphonic Acid, $\text{NH}(\text{SO}_3\text{H})\text{O}.\text{SO}_3\text{H}$, may be prepared from the corresponding trisulphonate by hydrolysis with a weak acid. In the presence of hydrogen chloride the SO_3H -group attached to the nitrogen atom may be eliminated, whereby *hydroxylamine-isomonosulphonic acid*, $\text{NH}_2.\text{O}.\text{SO}_3\text{H}$, is produced.⁶

Hydroxylamine-trisulphonic Acid.⁷—The potassium salt of this acid is formed by the interaction of potassium hydrogen sulphite and potassium nitrosodisulphonate, according to the equation :



¹ Raschig, *Schwefel- und Stickstoff-Studien*, 1924, p. 154.

² See also Claus, *Ann. Chem. Pharm. Lieb.*, 1871, 158, 85; Raschig, *ibid.*, 1887, 241, 166, 205; Divers and Haga, *Chem. News*, 1887, 56, 21.

³ Davy, *Elements of Chemical Philosophy* (London, 1812).

⁴ For the constitution of nitrososulphonates, etc., see Divers and Haga, *Trans. Chem. Soc.*, 1885, 47, 203; 1895, 67, 1098; Hantzsch, *Ber.*, 1905, 38, 1044, 3079. A compound, potassium "nitrososulphite" or potassium dinitrososulphonate, $\text{K}_2\text{N}_2\text{SO}_5$, prepared by the action of nitrous oxide on potassium sulphite, was described by Raschig, *Schwefel- und Stickstoff-Studien*, 1924, p. 108.

⁵ For a detailed account, see Raschig, *Schwefel- und Stickstoff-Studien*, 1924, p. 147; also Divers and Haga, *Trans. Chem. Soc.*, 1894, 65, 523; 1900, 77, 432, 440.

⁶ Raschig, *loc. cit.*, p. 132; *Ber.*, 1906, 39, 245; Haga, *Trans. Chem. Soc.*, 1906, 89, 240. The preparation of the potassium salt is described by Raschig, see *J. Chem. Soc.*, 1923, 124, A, ii., 161.

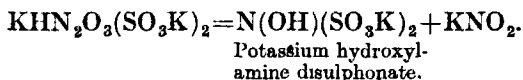
⁷ Raschig, *Schwefel- und Stickstoff-Studien*, 1924, p. 128.

Potassium hydroxylamine trisulphonate has the constitution $(\text{KSO}_3)_2 : \text{N.O.SO}_3\text{K}$.¹

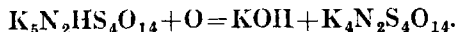
Dihydroxylamidodisulphonic Acid, $\text{N}(\text{OH})_2\text{SO}_3\text{H}$.—A basic salt of this acid having the composition $\text{N}(\text{OH})(\text{OK})\text{SO}_3\text{K}$ has been obtained as the first product of the interaction of sulphur dioxide with a concentrated alkaline solution of potassium nitrite.² The salt is alkaline in solution and with barium chloride yields a white precipitate, soluble in acids. Sulphuric acid liberates nitrous oxide from it.

Sulphazinic Acid, $\text{O} \begin{cases} \text{N}(\text{OH})(\text{SO}_3\text{H}) \\ \text{N}(\text{OH})(\text{SO}_3\text{H}) \end{cases}$.—The potassium salt of this

acid is formed when a stream of sulphur dioxide is passed through a concentrated solution of potassium nitrite.³ On standing, the salt decomposes to the hydroxylamine disulphonate and nitrite :



Sulphazotinic Acid, $\text{H}_6\text{N}_2\text{S}_4\text{O}_{14}$.—The potassium salt of this acid is obtained as in the preceding preparation by the action of sulphur dioxide on a solution of potassium nitrite, but in this case the solution is boiled.⁴ The salt consists of colourless, transparent, rhomboidal crystals, soluble in hot water, yielding an alkaline solution. Ammonia is evolved on heating the salt with soda-lime; concentrated acid liberates nitric oxide. The salt is decomposed by dilute acids with formation of sulphuric acid. On oxidation with lead dioxide or silver oxide at about 50°C . a solution of the salt becomes dark blue in colour, the potassium salt of dehydrosulphazotinic acid, $\text{K}_4\text{N}_2\text{S}_4\text{O}_{14}$, being formed :



Dehydrosulphazotinic Acid, $\text{H}_4\text{N}_2\text{S}_3\text{O}_{14}$.—The potassium salt deposits from the blue solution mentioned in the preceding preparation as bright yellow crystals. It is very unstable and is decomposed by water with formation of a new compound having the composition $\text{K}_3\text{N}_2\text{S}_3\text{O}_{10}$:



Nitrosulphonic Acid, Nitrosylsulphuric Acid or Nitroso-sulphuric Acid, $\text{NO}_2.\text{SO}_2.\text{OH}$.—In 1806, Clément and Désormes, during the manufacture of sulphuric acid by the lead chamber process, observed the formation of a crystalline solid, to which the names nitrosulphonic acid and nitrosylsulphuric acid were later given; the term "chamber crystals," however, is still commonly applied to this acid.⁶ The composition and nature of the acid were first investigated by Weber,⁷ and by Michaelis and Schumann.⁸

¹ See also Haga, *Trans. Chem. Soc.*, 1904, 85, 78.

² Frémy, *Ann. Chim. Phys.*, 1845, 15, [3], 408.

³ Frémy, *loc. cit.*

⁴ Frémy, *loc. cit.*

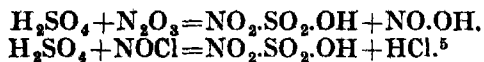
⁵ Frémy, *loc. cit.*; Claus, *Annalen*, 1871, 158, 85; Raschig, *loc. cit.*

⁶ Clément and Désormes, *Ann. Chim. Phys.*, 1806, 59, 329.

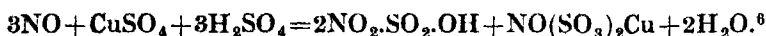
⁷ Weber, *J. prakt. Chem.*, 1862, 85, 423; *Ann. Phys. Chem.*, 1867, [n.], 130, 277.

⁸ Michaelis and Schumann, *Ber.*, 1874, 7, 1075.

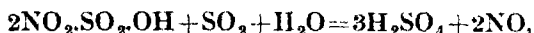
Formation.—When sulphur dioxide is passed into ice-cold fuming nitric acid, crystals of nitrosulphonic acid separate.¹ The acid is also obtained when sulphuric acid is treated with excess of nitrogen peroxide.² It is also formed by the interaction of sulphur dioxide and nitrogen peroxide both in the absence or presence of water,³ and by the addition in equimolecular proportion of liquid nitrogen tetroxide to chlorosulphonic acid in the absence of moisture.⁴ Sulphuric acid acts on either nitrous anhydride or nitrosyl chloride with formation of nitrosulphonic acid, according to the equations :



When nitric oxide is passed into a solution of cupric sulphate in concentrated sulphuric acid the following reaction occurs :



Properties.—Although nitrosulphonic acid may be obtained in the form of quadratic or rhombic prisms, it is more generally obtained as a leafy or feathery crystalline mass which has no definite melting-point but begins to decompose at 73° C., forming the anhydride (see later), nitrogen trioxide and sulphuric acid. No salts with the metals have been obtained. The acid is soluble in water with evolution of heat and decomposition into nitric oxide and sulphuric acid. The amount of nitric oxide formed increases on heating.⁷ If the solution is kept cold the products are sulphuric and nitrous acids, the latter undergoing further decomposition in its characteristic manner, the result being dependent on conditions. Cold concentrated sulphuric acid dissolves the crystals without decomposition. The reduction of a solution of nitrosulphonic acid in sulphuric acid by sulphur dioxide yields nitric oxide and sulphuric acid,



but in the presence of oxygen this reaction may be hindered or even checked, because the nitrosulphonic acid is re-formed by the interaction of sulphuric acid, nitric oxide and oxygen.

With phosphorus pentachloride nitrosulphonic acid yields chlorosulphonic acid and nitrosyl chloride :⁸



Sodium chloride and sodium bromide react with nitrosulphonic acid forming respectively nitrosyl chloride and bromide together with sodium hydrogen sulphate.⁹

¹ Weber, *loc. cit.*

² Gaultier de Claubry, *Ann. Chim. Phys.*, 1830, 45, 284; Muller, *Annalen*, 1862, 122, 1; Gay-Lussac, *Ann. Chim. Phys.*, 1816, [ii.], 1, 394; Rose, *Ann. Phys. Chem.*, 1842, [ii.], 50, 161; Lunge and Weintraub, *Zeitsch. angew. Chem.*, 1894, 7, 101.

³ Gaultier de Claubry, *loc. cit.*

⁴ Jones, Price and Webb, *J. Chem. Soc.*, 1929, p. 312.

⁵ Winkler, *Jahresber.*, 1869, p. 715.

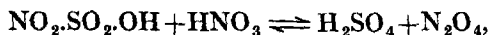
⁶ Sabatier, *Compt. rend.*, 1896, 123, 255. See also Sestini, *Bull. Soc. chim.*, 1868, [ii.], 10, 226; Lunge, *Ber.*, 1881, 14, 2196; Lunge and Berl, *Zeitsch. angew. Chem.*, 1906, 19, 890.

⁷ Elliott and others, *J. Chem. Soc.*, 1926, p. 1219; Frémy, *Compt. rend.*, 1870, 70, 61.

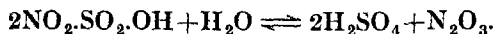
⁸ Michaels and Schumann, *Ber.*, 1874, 7, 1075.

⁹ Girard and Pabst, *Bull. Soc. chim.*, 1878, [ii.], 30, 531; Tilden, *Trans. Chem. Soc.*, 1874, 27, 630.

It is fairly generally believed that nitrosulphonic acid plays an important part in the "lead chamber" process for the manufacture of sulphuric acid (see p. 153). The vapour pressures of mixtures of sulphuric acid with nitrous or nitric acid or with both these acids, within the range occurring in the chambers, increase with the nitrogen acid content and with rise in temperature, and the total pressure is always higher than the sum of the individual pressures, especially when the sulphuric acid is concentrated. For nitric acid-sulphuric acid mixtures this may be explained¹ by the occurrence of the following reactions:



and



Constitution.—The formation of nitrosyl chloride or bromide by the action of the acid on sodium chloride or bromide is evidence in favour of the nitrosylsulphuric acid structure, $\text{ON} \cdot \text{O} \cdot \text{SO}_2 \cdot \text{OH}$. The

nitrosulphonic acid structure $\begin{array}{c} \text{O} \\ \diagup \\ \text{N} \cdot \text{SO}_2 \cdot \text{OH} \\ \diagdown \\ \text{O} \end{array}$ receives weighty support

from the fact that, in addition to the methods already given, the acid can also be obtained by the oxidising action of permonosulphuric acid on hydroxylamine-sulphonic acid, $\text{OH} \cdot \text{NH} \cdot \text{SO}_2 \cdot \text{OH}$, in which acid it is certain that the nitrogen is directly attached to sulphur.² The conflicting evidence is possibly due to the substance exhibiting tautomerism, in a similar manner to nitrous acid itself, which appears to be

able to assume the structures $\text{HO} \cdot \text{N} : \text{O}$ and $\text{H} \cdot \text{N} \begin{array}{c} \text{O} \\ \diagup \\ \diagdown \\ \text{O} \end{array}$ under varying

conditions; this view of the structure of nitrosulphonic acid receives marked confirmation in the action of the acid on certain organic substances, such as dimethylaniline, which give rise concurrently to a nitro- and a nitroso-derivative, the two forms of the acid appearing to act simultaneously and more or less independently. This result indicates the probability of an equilibrium between the two types of molecules $\text{NO}_2 \cdot \text{SO}_2 \cdot \text{OH}$ and $\text{ON} \cdot \text{O} \cdot \text{SO}_2 \cdot \text{OH}$.³

On the other hand, Elliott and his co-workers⁴ maintain that the evidence for the nitro- structure is unsatisfactory, and that the *p*-nitro-dimethylaniline produced with dimethylaniline is a secondary product obtained either by oxidation of the nitroso-compound or by direct nitration of the amine. The addition of ethyl hydrogen sulphate to a solution of nitrosulphonic acid in sulphuric acid does not yield nitro-ethane. Elliott suggests that the crystalline acid is essentially the nitroso- form, $\text{ON} \cdot \text{O} \cdot \text{SO}_2 \cdot \text{OH}$, but that in the molten condition and in sulphuric acid solution this form is in equilibrium with another of

structure $\text{O}_2\text{S} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \diagdown \quad \diagup \\ \text{O} \end{array} \text{N} \cdot \text{OH}$. This is in accordance with the behaviour

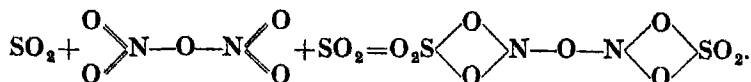
¹ Sanfouche and Rondier, *Compt. rend.*, 1928, 187, 291; *Bull. Soc. chim.*, 1928, [iv.], 43, 815.

² Raschig, *Zeitsch. angew. Chem.*, 1905, 18, 1302.

³ Biehringer and Borsum, *Ber.*, 1916, 49, 1402. See also Schlesinger and Salathe, *J. Amer. Chem. Soc.*, 1923, 45, 1863.

⁴ Elliott and others, *J. Chem. Soc.*, 1926, p. 1219.

of the acid on reduction and on heating, and also with the synthesis of the anhydride from sulphur dioxide and nitrogen pentoxide, thus :



Nitrosulphonyl (Nitrosylsulphuryl) Chloride, $\text{NO}_2 \cdot \text{SO}_2 \text{Cl}$.—The acid chloride structurally derived from nitrosulphonic acid can be obtained by the interaction of thionyl chloride (or less simply chlorosulphonic acid) and silver nitrate :



It may also be obtained by the action of nitrosyl chloride on sulphuric anhydride. It is a white, leafy, crystalline mass, somewhat resembling stearic acid in appearance. It is decomposed by moist air with formation of sulphuric, hydrochloric and nitric acids.¹

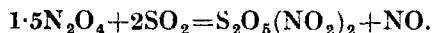
Nitrosulphonic Anhydride, $\text{S}_2\text{O}_5(\text{NO}_2)_2$.—Nitrosulphonic anhydride, or nitrous-pyrosulphuric anhydride (the choice of name depending on the view entertained as to the structure of the NO_2 -group), is formed during the decomposition of nitrosulphonic acid by heat (p. 248),² but it may more conveniently be obtained by the action of dry nitric oxide on sulphur trioxide :³



It is also formed by the action of nitrogen peroxide on liquid sulphur dioxide under pressure :⁴



With both reactants in the liquid state the reaction proceeds according to the equation :⁵



The pressure increases slowly at first but after a time a considerable increase suddenly occurs. The anhydride is also formed when the two gases react, only very slowly at ordinary temperatures, but more rapidly at higher temperatures. The reaction is never complete but goes somewhat further in the presence of platinised asbestos.⁶ The anhydride may also be prepared by the action of liquid nitrogen tetroxide on pyrosulphuric acid or pyrosulphuryl chloride.

Nitrosulphonic anhydride is a white, crystalline solid, of density 2.14. On heating it undergoes partial decomposition ;⁷ it begins to melt at 217° C. to a yellow liquid and distils at about 360° C. The heat of formation, calculated from the heat of dissolution in potassium hydroxide, is 112 Calories :

¹ Thorpe, *Trans. Chem. Soc.*, 1882, 41, 297.

² Michaelis and Schumann, *Ber.*, 1874, 7, 1075.

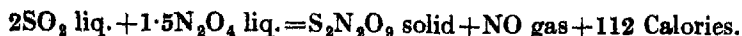
³ Rose, *Ann. Phys. Chem.*, 1839, [ii.], 47, 605 ; Brüning, *Annalen*, 1856, 98, 377.

⁴ Prevostaye, *Ann. Chim. Phys.*, 1840, 73, 362. See also Morren, *ibid.*, 1865, [iv.], 4, 293 ; Weber, *Ann. Phys. Chem.*, 1871, [ii.], 142, 602 ; 1864, [ii.], 123, 337.

⁵ Briner, Lunge and van der Wijk, *Helv. Chim. Acta*, 1928, 11, 1125.

⁶ Briner and others, *loc. cit.* See also Manchot and Schmid, *Ber.*, 1929, 62, [B], 1261.

⁷ Jones, Price and Webb, *J. Chem. Soc.*, 1929, p. 312 ; Briner and others, *loc. cit.*



As would be expected from a substance of this nature, water causes rapid decomposition into sulphuric acid and the decomposition products of nitrous acid, whilst sulphuric acid dissolves the substance with formation of nitrosulphonic acid, which crystallises on cooling. With sulphur trioxide the anhydride yields a stable complex of composition $2(\text{S}_2\text{N}_2\text{O}_6) \cdot \text{SO}_3$.¹ Gaseous ammonia causes the anhydride to melt and decompose slowly with formation of nitrogen and ammonium hydrogen sulphate :

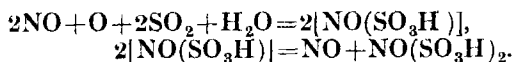


The modes of preparation, particularly from pyrosulphuric acid and pyrosulphuryl chloride, and the general properties of nitrosulphonic anhydride, suggest the structure $^2 \text{O} \cdot \text{NO} \cdot \text{SO}_2 \cdot \text{O} \cdot \text{SO}_2 \cdot \text{O} \cdot \text{NO}$.

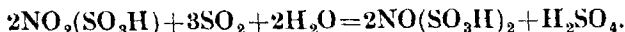
Nitrosulphuric Acid, $\text{N}_2\text{O}_5 \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$, may be obtained by the prolonged action of the vapour of sulphur trioxide on concentrated nitric acid. It forms brilliant white crystals which on heating yield brown vapours and a sublimate of nitrosulphonic acid. It is soluble in water, yielding a mixture of nitric and sulphuric acids.³

According to Somiya,⁴ the gradual addition of fuming sulphuric acid to an aqueous mixture of sulphuric and nitric acids results in two successive temperature maxima being reached, the second being the less well-defined. The first corresponds with the formation of sulphuric acid from the free sulphur trioxide and the compound $\text{SO}_3 \cdot \text{HNO}_3$ or $\text{OH} \cdot \text{SO}_2 \cdot \text{ONO}_2$, and the second with conversion of the latter into $\text{N}_2\text{O}_5 \cdot 4\text{SO}_3$.

Nitrosodisulphonic Acid, Peroxylaminic Acid, or Sulphazilic Acid, $\text{NO}(\text{SO}_3\text{H})_2$.—This is only known in solution ; it may be obtained by the passage of equal volumes of nitric oxide and air into a cooled saturated solution of sulphur dioxide in sulphuric acid. It forms an intense bluish-violet solution :⁵



It is also formed by passing sulphur dioxide into a solution of sodium nitrite in sulphuric acid :⁶



Nitrosodisulphonic acid decomposes spontaneously into sulphuric acid, sulphur dioxide and nitric oxide. Its solution is rapidly decolorised on shaking with air or on mixing with hydrogen peroxide, permmono- or perdisulphuric acid, nitric acid, chlorine or potassium chlorate. Most metallic oxides and carbonates decompose the solution, being converted into sulphates.⁷

Sulphonitronic Acid or "*Purple Acid*."—For a considerable time

¹ Jones, Price and Webb, *loc. cit.*

² Jones, Price and Webb, *loc. cit.*

³ Weber, *Ann. Phys. Chem.*, 1871, [ii.], 142, 602.

⁴ Somiya, *Chem. News*, 1928, 137, 14.

⁵ Sabatier, *Compt. rend.*, 1896, 122, 1479–1537.

⁶ Sabatier, *loc. cit.*

⁷ See also Haga, *Trans. Chem. Soc.*, 1904, 85, 78, 84 ; Divers, *ibid.*, p. 108 ; Hantzsch, *Ber.*, 1905, 38, 3079 ; Raschig, *Zeitsch. anorg. Chem.*, 1905, 18, 1304.

the existence of an unstable compound which yields a purple solution in sulphuric acid has been known. Of various names which have been suggested for this compound, the designation "sulphonitronic acid" ¹ possesses the advantage of indicating the nature of the chief constituent elements without committing itself to any definite conception of the structure or constitution. The acid has been regarded as a derivative of quadrivalent nitrogen, viz. "nitrosulphonic acid," $O : N(OH).SO_2.OH$,² or peroxyaminic acid, $NO(SO_2.OH)_2$ ³ (see p. 251). Unfortunately the question of the actual constitution is still undecided, and even the composition is uncertain. According to more recent investigations it appears probable that the "acid" is either an oxide of nitrogen ⁴ intermediate between NO and N_2O_3 , or a compound of sulphuric acid with such an oxide.⁵ On account of this uncertainty the compound is frequently referred to merely as "purple acid" (also "blue acid" and "violet acid"). It has possibly acquired undue importance on account of its occurrence as an intermediate product in the "lead chamber" process for the manufacture of sulphuric acid.

Formation.—The coloured solution in sulphuric acid is obtainable by passing nitrogen dioxide with air into a saturated solution of sulphur dioxide in diluted sulphuric acid (1 : 1 by volume) at 0° C. It can also be formed by the addition of sodium hydrogen sulphite to a solution of nitrosulphonic (nitrosylsulphuric) acid, produced by dissolving sodium nitrite in slightly diluted sulphuric acid. These methods depend on the reduction of the nitrosulphonic acid by sulphurous acid or sulphur dioxide; ⁶ the reduction can also be effected by metals, *e.g.* mercury.

Properties.—The blue solution is unstable and decomposes slowly, with formation of sulphuric acid, sulphur dioxide and nitrogen dioxide. When shaken with air or submitted to oxidation by chlorine, nitric acid or hydrogen peroxide, conversion into nitrosulphonic acid is effected, brown fumes being liberated. Dilution with water also destroys the coloured substance. If strongly cooled, the solution changes to an intense red, so that if a solution is too weak to possess a marked colour at the ordinary temperature, the presence of the "purple acid" can easily be detected by cooling in a mixture of acetone and solid carbon dioxide.

Certain of the salts in solution have a stronger colour than the acid, and in some cases are more stable; thus, a deep blue solution of the copper salt may be obtained by the reduction of nitrosulphonic acid (in sulphuric acid) by mercury in the presence of copper. A suggestion has been made ⁷ that the colour in the "brown ring" test for a nitrate is due to the formation of the ferrous salt of "purple acid," but this is improbable.⁸

Sulphates of Hydroxylamine.—The normal sulphate of hydroxylamine, $(NH_2OH)_2.H_2SO_4$, is formed by evaporation of hydroxylamine

¹ Lunge and Berl, *Zeitsch. angew. Chem.*, 1906, 19, 807, 857, 881; 1907, 20, 1713, 2074.

² Raschig, *ibid.*, 1905, 18, 1303; *J. Soc. Chem. Ind.*, 1911, 30, 166.

³ Sabatier, *Bull. Soc. chim.*, 1897, [iii.], 17, 782.

⁴ Manchot, König and Reimlinger, *Ber.*, 1926, 59, [B], 2672.

⁵ Manchot, *Zeitsch. angew. Chem.*, 1910, 23, 2113; 1911, 24, 13; 1912, 25, 1055. See also Diversi, *J. Soc. Chem. Ind.*, 1911, 30, 594; *Trans. Chem. Soc.*, 1904, 85, 108; Wentzki, *Zeitsch. angew. Chem.*, 1911, 24, 392, 1468.

⁶ Trautz, *Zeitsch. physikal. Chem.*, 1903, 47, 601.

⁷ Raschig, *loc. cit.*; also *Ber.*, 1907, 40, 4580.

⁸ Manchot, *loc. cit.*

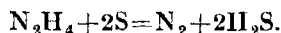
hydrochloride with the calculated amount of sulphuric acid. It forms large monoclinic prisms, melting at 170°C . With the sulphates of iron, aluminium and chromium, alums are obtained, while with magnesium sulphate a double salt is obtained of the type $\text{MgSO}_4 \cdot [\text{NH}_3(\text{OH})]_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$.¹

The *acid sulphate* of hydroxylamine, $\text{NH}_2\text{OH} \cdot \text{H}_2\text{SO}_4$, is obtained as long deliquescent prisms when hydroxylamine hydrochloride which has been treated with the quantity of sulphuric acid necessary to form the acid salt is heated for some time to expel all the hydrogen chloride.

Hydroxylamine Dithionate, $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{S}_2\text{O}_6$, is obtained by the action of hydroxylamine sulphate on barium dithionate. At 120°C . it is converted into hydroxylamine sulphate and sulphur dioxide. It is isomeric with ammonium perdisulphate.² Hydroxylamine amidosulphonate, $\text{NH}_2\text{OH} \cdot \text{NH}_2 \cdot \text{SO}_3\text{H}$, is isomeric with ammonium oxyamidodisulphonate, $\text{NH}(\text{OH})\text{SO}_3\text{NH}_2$, and with hydrazine sulphate, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$.³

Sulphur Compounds of Hydrazine.

Sulphur readily dissolves both in hydrazine and hydrazine hydrate with evolution of nitrogen :



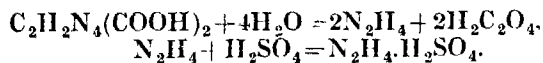
An unstable **hydrazine hydrosulphide** remains in solution.

With hydrogen sulphide hydrazine forms an addition product of undetermined composition.⁴

Sulphur dioxide, when slowly passed into a cooled alcoholic solution of hydrazine, yields the **hydrazine salt of hydrazine disulphinic acid**, $\text{N}_2\text{H}_4(\text{SO}_2 \cdot \text{N}_2\text{H}_4)_2$.⁵ When the gas is passed into an aqueous solution of hydrazine hydrate, **hydrazine pyrosulphite**, $(\text{N}_2\text{H}_4)_2 \cdot \text{H}_2\text{S}_2\text{O}_5$, is formed, which, on neutralisation with hydrazine hydrate, yields **hydrazine sulphite**, $(\text{N}_2\text{H}_4)_2 \cdot \text{H}_2\text{SO}_3$.⁶

Sulphur trioxide is immediately reduced by hydrazine under all conditions, sulphur sesquioxide, S_2O_3 , being formed.⁷

When hydrazine hydrate is neutralised with sulphuric acid, **dihydrazine sulphate**, $(\text{N}_2\text{H}_4)_2 \cdot \text{H}_2\text{SO}_4$, is obtained.⁸ **Hydrazine sulphate**, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$, is obtained when *bis*-diazooacetic acid, $\text{C}_2\text{H}_2\text{N}_4(\text{COOH})_2$, is warmed with sulphuric acid :⁹



A mixture of hydrazine sulphate and potassium bromide is an efficient substitute for stannous chloride in the prevention of the decomposition of hydrogen sulphide by ferric chloride.¹⁰

¹ Preibisch, *J. prakt. Chem.*, 1873, [2], 7, 480. See also Divers and Haga, *Trans. Chem. Soc.*, 1896, 69, 1665.

² Sabanéeff, *Zetsch. anorg. Chem.*, 1898, 17, 480.

³ Sabanéeff, *loc. cit.* For the action of sulphites and hydrogen sulphites on hydroxylamine, see Raschig, *Schwefel- und Stickstoff-Studien*, 1924, p. 225.

⁴ Ephraim and Piotrowski, *Ber.*, 1911, 44, 386.

⁵ Ephraim and Piotrowski, *loc. cit.*

⁶ Sabanéeff and Speransky, *Zeitach. anorg. Chem.*, 1899, 20, 21.

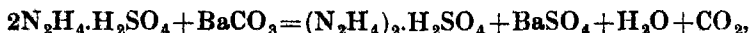
⁷ Ephraim and Piotrowski, *loc. cit.*

⁸ Curtius, *J. prakt. Chem.*, 1891, [2], 44, 101.

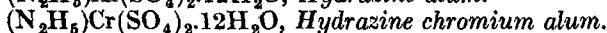
⁹ Curtius and Jay, *Ber.*, 1890, 23, 740.

¹⁰ Scheidler, *Chem. Zeit.*, 1919, 41, 580.

When hydrazine sulphate is treated with barium carbonate in hot solution, dihydrazine sulphate forms according to the equation:



and can be separated as the monohydrate by crystallisation at 0°C . Dihydrazine sulphate forms double salts with the sulphates of certain metals and also forms compounds analogous to the alums:¹



Hydrazine Dithionate, $\text{N}_2\text{H}_4\cdot\text{H}_2\text{S}_2\text{O}_6$, a polymer of amidosulphonic acid, may be prepared by the interaction of hydrazine sulphate and barium dithionate. It is obtained as large crystals. On evaporation over sulphuric acid it decomposes with separation of sulphuric anhydride and is converted into a mixture of hydrazine sulphate and secondary hydrazine dithionate, $(\text{N}_2\text{H}_4)_2\cdot\text{H}_2\text{S}_2\text{O}_6$.²

Hydrazine Amidosulphonate, $\text{NH}_2\cdot\text{SO}_3\cdot\text{N}_2\text{H}_5$, may be obtained by adding barium amidosulphonate to a neutral solution of hydrazine sulphate. It is a crystalline solid, slightly soluble in water.³

SULPHUR AND CARBON.

When a mixture of carbon and sulphur is heated, chemical combination occurs. Sulphur is absorbed by the carbon, and according to Wibaut⁴ a product which is probably a complex of carbon with a sulphide of carbon is first formed, carbon disulphide being gradually evolved as the temperature rises (see p. 256). The solid complex is practically non-volatile at 1000°C . and prolonged boiling with toluene fails to extract any sulphur. The quantity of sulphur retained seems to depend on the nature of the carbon and on the extent of its surface; the crystalline forms, diamond and graphite, do not fix any sulphur under these conditions. These results are analogous to those obtained with carbon and oxygen.⁵ The individual sulphur atoms absorbed by the amorphous carbon appear to be held with varying tenacity, as evidenced by the gradual loss when the substance is heated at rising temperatures in vacuum or hydrogen. Part at least of the sulphur appears to be in actual chemical combination with the carbon.⁶

In addition to the well-known disulphide several other sulphides of carbon have been described,⁷ although probably they are not in every case separate chemical entities. The existence of the compound C_4S , for example, is doubtful.⁸ A sulphide of composition C_8S_2 results,

¹ For an account of the sulphates of hydrazine, see Sommer and Weise, *Zeitsch. anorg. Chem.*, 1916, 94, 51.

² Sabanéeff, *Zeitsch. anorg. Chem.*, 1899, 20, 21.

³ Sabanéeff, *loc. cit.*

⁴ Wibaut, *Proc. K. Akad. Wetensch. Amsterdam*, 1921, 24, 92; with van der Kam, *ibid.*, 1929, 32, 501; *Rec. Trav. chim.*, 1922, 41, 153.

⁵ Rhead and Wheeler, *Trans. Chem. Soc.*, 1913, 103, 461; 1912, 101, 846. See also this Series, Vol. VII., Part I., and Lowry and Hulett, *J. Amer. Chem. Soc.*, 1920, 42, 1408.

⁶ For the forms in which sulphur exists in coke, see Powell, *J. Amer. Chem. Soc.*, 1923, 45, 1.

⁷ See, for example, Wibaut, *Zeitsch. angew. Chem.*, 1927, 40, 1136.

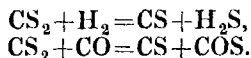
⁸ See Low, *Jahresber.*, 1867, p. 157; Berzelius, *Ann. Phys. Chem.*, 1826, 6, 444.

according to Raab,¹ from the action of sodium on carbon disulphide; the dark crust which is formed yields this sulphide, on treatment with acids, as a reddish-brown precipitate, insoluble in carbon disulphide.

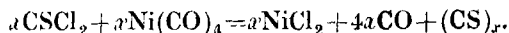
Carbon Subsulphide, C_3S_2 .—This is the analogue of the suboxide, C_3O_2 . It is a deep red, tear-exciting liquid, obtained by Lengyl² as one of the products when carbon disulphide vapour was submitted to the action of an electric arc. With bromine it forms a yellow solid of composition $C_3S_2Br_6$. Carbon subsulphide has also been prepared³ by striking an arc between a carbon cathode and an anode consisting of antimony containing 7 per cent. of carbon, placed beneath the surface of liquid carbon disulphide. The constitutional formula $S:C:C:C:S$ is attributed to this compound.

A sulphide C_2S_3 is described by Low⁴ as a brown, odourless, amorphous substance, only sparingly soluble in carbon disulphide. It is said to be formed during the thermal decomposition of the disulphide⁵ (see p. 261).

Carbon Monosulphide, CS .—This sulphur analogue of carbon monoxide is described as resulting⁶ on passing carbon disulphide vapour over spongy platinum, pumice stone or red-hot charcoal. It is also formed by the action of the silent electric discharge⁷ on carbon disulphide or on a mixture of the latter with either hydrogen or carbon monoxide, thus :



Thiocarbonyl chloride reacts rapidly with nickel carbonyl at the ordinary temperature according to the equation :



After the nickel chloride has been extracted from the solid product by water, a brown substance remains which has the empirical formula CS , but which, on account of its being a non-volatile solid, must be a polymer, $(CS)_x$. According to Dewar and Jones,⁸ carbon monosulphide is an endothermic gas which is condensable by liquid air and which rapidly polymerises to $(CS)_x$ at atmospheric temperature.

Carbon Disulphide and its Derivatives.

Carbon Disulphide, CS_2 , is formed when carbon and sulphur are heated together and is consequently produced when coal containing iron pyrites is distilled.⁹ It was discovered accidentally in this way by Lampadius¹⁰ in 1796 and rediscovered in 1802 by Clément and Désormes. Besides occurring in small quantity in crude coal gas, from which it is

¹ Raab, *Bull. Soc. chim.*, 1872, 15, 41.

² Lengyl, *Ber.*, 1894, 26, 2960.

³ Stock and Prætorius, *ibid.*, 1912, 45, 3568.

⁴ Low, *Jahresber.*, 1886, p. 119; 1867, p. 157.

⁵ Arctowski, *Zeitsch. anorg. Chem.*, 1895, 8, 314.

⁶ Baudrimont, *Compt. rend.*, 1857, 44, 1000.

⁷ Dewar and Jones, *Proc. Roy. Soc.*, 1910, [A], 83, 408, 526.

⁸ Dewar and Jones, *loc. cit.*

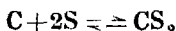
⁹ See Huff, *Ind. Eng. Chem.*, 1926, 18, 357.

¹⁰ Lampadius, *Gehlen's Allg. J. Chem.*, 1796, 11, 192.

usually eliminated, carbon disulphide is also found in crude petroleum and in mustard oil.

Preparation.—Carbon disulphide is prepared by passing sulphur vapour over red hot charcoal. The preparation may be carried out on a small scale by heating pieces of charcoal in a combustion tube placed in a furnace slightly tilted, a Liebig potash bulb, immersed in ice, being attached to the lower end of the tube, and small pieces of sulphur introduced into the upper end of the tube which is then closed with a cork. Sulphur vapour passes over the red-hot charcoal and impure carbon disulphide containing sulphur in solution is gradually formed and collects in the cooled receiver.

The reversible reaction



has been studied at 800° to 1100° C. by Koref.¹ It has been suggested² that the formation of carbon disulphide is preceded by that of a solid

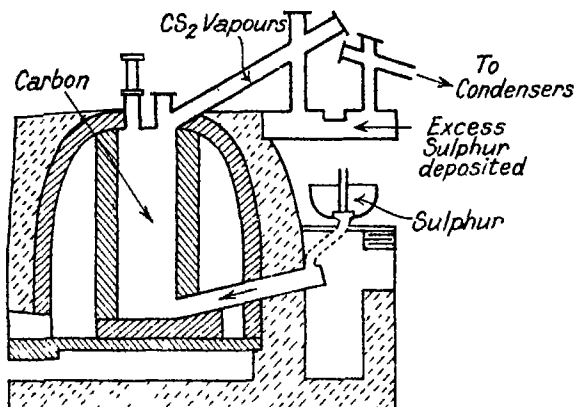


FIG. 14.—Manufacture of Carbon Disulphide by the action of Sulphur Vapour on Carbon.

sulphur-carbon complex, just as the oxidation of carbon is believed to be preceded by the formation of a complex C_xO_y ³ (see p. 254).

For the manufacture of carbon disulphide on the large scale, the charcoal is contained in a large vertical cast-iron cylinder, ten to twelve feet high and from one to two feet in diameter. This cylinder is surrounded by brickwork and heated by a fire beneath. The sulphur is introduced through a hopper connected with a side tube at the base of the cylinder. The carbon disulphide vapour is led away from the top of the cylinder through a pipe, the end of which dips under water, where most of the product condenses. Beyond the water condenser is a series of tubes in which condensation is completed. Hydrogen sulphide, one of the impurities, escapes condensation and passes on, being subsequently absorbed in slaked lime.⁴

¹ Koref, *Zeitsch. anorg. Chem.*, 1910, 66, 73.

² Wibaut, *loc. cit.*; Huff and Holtz, *Ind. Eng. Chem.*, 1927, 19, 1268; *Proc. Amer. Gas Assoc.*, 1927, p. 1431.

³ Rhead and Wheeler, *Trans. Chem. Soc.*, 1913, 103, 461, 1912, 101, 846.

⁴ See further, Schulz, *German Patents*, 407656, 438037 (1925); Stephens, *British Patent*, 261990 (1926); Siedler, *U.S. Patent*, 1615659 (1927).

Instead of an iron cylinder furnace, retorts made of refractory material are sometimes employed. The water condensers may be of the open tank type, a layer of about six inches of water on top of the disulphide affording a thoroughly efficient seal.¹ The liquid may be purified from dissolved sulphur by steam distillation. A modern method for the final rectification of the carbon disulphide² consists in the continuous distillation of the crude liquid in two similar fractionating columns fitted with reflux condensers. The first column is maintained at a temperature just above the melting-point of sulphur and fed with crude carbon disulphide from above, whilst the second is kept at a temperature slightly above the boiling-point of pure carbon disulphide and fed at the top with the purified liquid from the first column. Condensation of the vapours leaving the lower end of the second column yields pure carbon disulphide. The waste gases (hydrogen sulphide, etc.) escape from the reflux condensers and are condensed by further cooling, any carbon disulphide obtained being passed back to the first column. The sulphur which separates is drawn off as liquid from the still of the first column.³

A thermo-electrical process for the production of carbon disulphide from its elements is also largely employed, especially in America.⁴

The type of furnace generally employed is shown diagrammatically in fig. 15. The heat emanated from the electrodes E_1 and E_2 melts and ultimately vaporises the sulphur, which then passes up through the tower of charcoal. The furnace is self-regulating in that if it becomes too hot, the sulphur, melting at a more rapid rate than it volatilises, rises up over the electrodes, thus reducing or cutting off the current. Two-phase alternating current is employed, and the efficiency exceeds 40 per cent.

The sulphur may be evaporated and superheated either in the

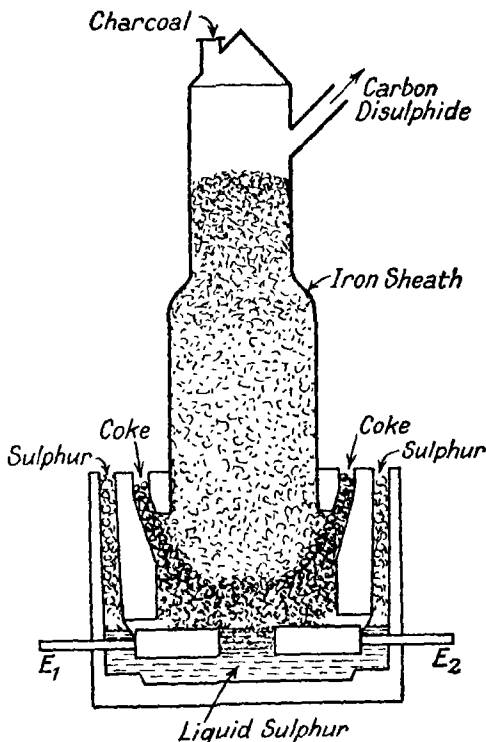


FIG. 15.—Electric Furnace for the Production of Carbon Disulphide.

¹ Caddick, *Chemical Age*, 1928, 19, 536.

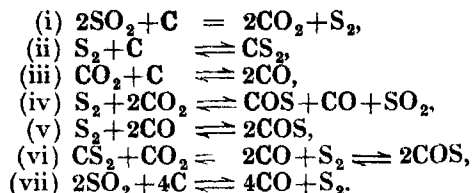
² See I. G. Farbenind. A.-G., *Assecs. of P. Siedler and E. Schulte, German Patent, 439766* (1925), and of Chem. Fabr. Griesheim-Elektron, *British Patent, 260236* (1926).

³ See also Legeler and Esselmann, *British Patent, 254676* (1925).

⁴ See Taylor, *Zeitsch. Elektrochem.*, 1903, 9, 679, 982; also Allmand and Ellingham *Applied Electro-chemistry* (Arnold, 1924), p. 666. See also Buchner, *German Patent, 433521* (1925).

reaction chamber itself or in an attached chamber before it is brought into contact with the charcoal.

Carbon disulphide may also be formed by the action of sulphur dioxide on carbon.¹ When sulphur dioxide is led over red-hot charcoal which has previously been freed from hydrogen by heating it in a current of chlorine, the following reactions can occur :—



The free sulphur in the issuing gas may be removed by condensation and filtration through glass wool. Carbon disulphide vapour may be absorbed in ethereal triethylphosphine. The maximum formation of the disulphide is at 850° to 900° C., the sulphur from the sulphur dioxide then being distributed as follows :—

Carbon disulphide	.	.	35 per cent.
Carbonyl sulphide	.	.	55 "
Free sulphur	.	.	10 "

This process is useless as a technical method of making carbon disulphide.

Crude carbon disulphide has a very offensive odour due to the presence of organic sulphur compounds; sulphur is also contained in solution and is left behind on redistillation. Organic impurities may be eliminated by distilling over fat, which retains them. Contact with mercury, fuming nitric acid, corrosive sublimate or solid potassium permanganate serves the same purpose. Commercial carbon disulphide may be freed from hydrocarbons by shaking for twenty-four hours at 35° to 40° C. with a saturated solution of sodium sulphide. The solution of sodium thiocarbonate obtained is treated with the calculated amount of copper sulphate solution, the resulting copper thiocarbonate being decomposed with steam. The product is dried over phosphorus pentoxide.

When sulphur is heated with acetylene at temperatures up to 650° C. and the products condensed, a brown oil is obtained which contains 77 to 88 per cent. of carbon disulphide, with some thiophen and thiophen (see p. 262). The optimum temperature for producing the latter compounds is 500° C.²

When calcium carbide and sulphur are heated together at 270° C. carbon disulphide in about 20 per cent. yield and considerable quantities of carbon are produced.³ At higher temperatures the amount of carbon disulphide diminishes, only traces being detected at 500° C.

Physical Properties.—Pure carbon disulphide is a colourless, mobile, highly refractive liquid with a pleasant odour resembling that of

¹ Rassow and Hoffmann, *J. prakt. Chem.*, 1922, [ii.], 104, 207.

² Peel and Robinson, *J. Chem. Soc.*, 1928, p. 2068; Briscoe and Peel, *ibid.*, p. 1741. See also Meyer and Sandmeyer, *Ber.*, 1883, 16, 2176; Capelle, *Bull. Soc. chim.*, 1908, 4, 150; de Coninck, *Bull. Acad. roy. Belg.*, 1908, p. 305.

³ Biesalski and van Eck, *Zeitsch. angew. Chem.*, 1928, 41, 720.

chloroform. Its density at 0° C. according to Thorpe¹ is 1.2928; according to Wüllner² the density at t° C. can be calculated from the formula

$$D_0^t = 1.29866 - 0.001506t.$$

Carbon disulphide vapour appears to be associated to a small extent. When the vapour and ether vapour are mixed at constant volume at 80° C. under atmospheric pressure, the increase of pressure observed indicates previous association of the carbon disulphide to the extent of 0.14 per cent., whilst vapour density determinations by Dumas' method give results corresponding with 2 per cent. association.³

The boiling-point at 760 mm. pressure is 46.25° C.⁴ According to Regnault⁵ the vapour pressures at different temperatures are as follows:—

Temp., ° C.	Vapour Pressure, mm.	Temp., ° C.	Vapour Pressure, mm.	Temp., ° C.	Vapour Pressure, mm.
-20	47.3	40	617.53	100	3325.15
-10	79.44	50	857.07	110	4164.06
0	127.91	60	1164.51	120	5148.79
10	198.46	70	1552.09	130	6291.60
20	298.03	80	2032.53	140	7603.96
30	434.62	90	2619.08	150	9095.94

The constants for van der Waals' equation are ⁶ $a=0.02166$, $b=0.003209$, and the critical temperature and pressure are, respectively, 277.68° C. and 78.14 atmospheres.

At very low temperatures carbon disulphide solidifies to a crystalline mass which melts at -112.97° C.⁷ The crystallisation may be accompanied by the emission of small sparks.⁸ At -185° C. the crystals are tetragonal.⁹ The heat of fusion, deduced from determinations of the freezing-points of dilute solutions in certain organic solvents,¹⁰ is 660 calories. The fusion curve showing the connection between pressure and melting-point has been determined.¹¹

The total heat of vaporisation¹² (λ) of carbon disulphide at 0° C. into vapour at t° C. is given by the expression

$$\lambda = 89.5 + 0.16998t - 0.0010161t^2 + 0.0000033245t^3 \text{ calories per kilogram,}$$

¹ Thorpe, *Trans. Chem. Soc.*, 1880, 37, 364.

² Wüllner, *Pogg. Annalen*, 1868, 133, 19.

³ Schulze, *Zeitsch. anorg. Chem.*, 1921, 118, 223. See also V. and C. Meyer, *Ber.*, 1879, 11, 2257.

⁴ von Unruh, *Zeitsch. anorg. Chem.*, 1902, 32, 407.

⁵ Regnault, *Mém. de l'Acad.*, 1862, 26, 339.

⁶ Hannay, *Proc. Roy. Soc.*, 1882, 33, 314.

⁷ Keyes, Townshend and Young, *J. Math. Phys. Mass. Inst. Tech.*, 1922, 1, 243; Holborn and Wien, *Zeitsch. physikal. Chem.*, 1903, 44, 80. Earlier values are -108.6° C. (Carrara and Coppadoro, *ibid.*, 1903, 44, 379) and -110° C. (Wroblewski and Olszewski, *Compt. rend.*, 1883, 96, 1142).

⁸ See Anschütz, *Ber.*, 1926, 59, [B], 455.

⁹ For the crystal structure of solid carbon disulphide, see de Smedt, *Natuurwetensch. Tijdschr.*, 1926, 8, 13.

¹⁰ Mitsukuri, *Bull. Chem. Soc. Japan*, 1926, 1, 30.

¹¹ See Tammann, *Zeitsch. physikal. Chem.*, 1912, 81, 187.

¹² Winkelmann, *Ann. Physik*, 1880, 9, 208, 358.

whilst the latent heat of vaporisation (l) of liquid at t° C. into vapour at t° C. is given by

$$l = 89.5 - 0.06530t - 0.0010979t^2 + 0.0000034245t^3 \text{ calories per kilogram.}$$

The constant, K , for the molecular elevation of the boiling-point of carbon disulphide is $23.7.1$. The specific heat, C , of liquid carbon disulphide is given by ²

$$C_{\text{liq.}} = 0.2352 + 0.000162t,$$

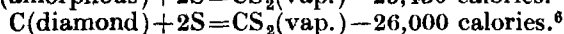
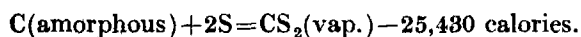
and for the vapour at 86° to 190° C. is 0.1596 , whilst the ratio $\frac{C_p}{C_v}$ at 99.7° C. is 1.234 .³

Towards light, carbon disulphide possesses high refractive and dispersive powers, and in these properties is exceeded only by methylene iodide, bromonaphthalene and phenyl mustard oil. On this account it is used for filling hollow glass prisms for the production of spectra.⁴

The following are the refractive indices ⁵ for lines of different wavelengths of the visible spectrum at 0° C. and 20° C. :—

Wave-length.	Refractive Index at 0° C.	Refractive Index at 20° C.
589.81 $\mu\mu$ (D)	1.64362	1.62761
588.85 "	1.65508	1.63877
480.01 "	1.67131	1.65466
441.59 "	1.68850	1.67185
394.41 "	1.71989	1.70180

Carbon disulphide is an endothermic compound, its heats of formation as vapour from rhombic sulphur and amorphous carbon or diamond being, respectively, $-25,430$ calories or $-26,000$ calories :



Carbon disulphide is an excellent solvent for fats and resins ; it is employed technically for the extraction of vegetable fats and oils and for removing fats from wool. It dissolves rubber, camphor and other organic substances, as well as iodine, sulphur, phosphorus and aluminium bromide.⁷

The disulphide is slightly soluble in water, the solubility diminishing with rising temperature like that of a gas. One hundred cubic centimetres of water dissolve the following quantities of carbon disulphide at the temperatures indicated : ⁸

¹ Beckmann, *Zetsch. physikal. Chem.*, 1890, 6, 437.

² Regnault, *Mém. de l'Acad.*, 1862, 26, 1, 262.

³ Stevens, *Ann. Physik*, 1902, [iv.], 7, 285.

⁴ For the refraction and dispersion of gaseous carbon disulphide, see Lowery, *Proc. Physical Soc.*, 1926, 38, 470.

⁵ Flatow, *Ann. Physik*, 1903, [iv.], 12, 85.

⁶ Thomsen, *Zeitsch. physikal. Chem.*, 1905, 52, 348.

⁷ See Kaveler and Monroe, *J. Amer. Chem. Soc.*, 1928, 50, 2421.

⁸ Chancel and Parmentier, *Compt. rend.*, 1885, 100, 773.

Temp., °C.	0	10	20	30	40	49
Grams CS ₂	0.204	0.194	0.179	0.155	0.111	0.014.

Clear aqueous solutions of considerable concentration may, however, be obtained, and are produced commercially,¹ by the addition of soap and an alcohol; thus a solution containing 5 per cent. of carbon disulphide, 2.3 per cent. of soap and 4.2 per cent. of butyl alcohol is stable. Amyl alcohol may also be used. 100 c.c. of carbon disulphide dissolve 0.974 c.c. of water at 22° C.²

Carbon disulphide absorbs ultra-violet rays, a maximum absorption being reached when λ is approximately 3250 Å.³ The "chemical constant" is given by Nernst as 3.1.

Chemical Properties.—Carbon disulphide is not easily decomposed by heat and no change is observed when it is passed through a tube at 400° C. Decomposition may be started by detonation with mercury fulminate, but it is not propagated through the vapour.⁴ Under the influence of sunlight the disulphide may be decomposed into sulphur and a lower sulphide of carbon.⁵ According to Berthelot this decomposition is partially due to the oxygen of the air and is not produced by diffused light.⁶ Dissociation to carbon and sulphur or lower sulphides, which is considerable at high temperatures, is promoted by the presence of metals or gases with which the sulphur can combine (see p. 255). Decomposition also occurs under the influence of the electric arc, electric sparks or the silent electric discharge (see p. 255).

Carbon disulphide burns in air with a blue flame, producing carbon dioxide and sulphur dioxide. Moisture is not necessary for the combustion.⁷ It inflames at a lower temperature than ether.

When a stream of air or oxygen laden with carbon disulphide vapour is passed through a tube heated to about 200° C., a gentle phosphorescent combustion is observed and a reddish-brown deposit, carbon monosulphide, separates,⁸ sulphur dioxide also being formed. The transition from this state to actual rapid combustion is not sharp, so that no definite ignition-point can be assigned to such mixtures.⁹ There is little difference between the spectrum of the cool phosphorescent flame and that of the normal flame of carbon disulphide, except in the distribution of intensity, but a group of closely spaced bands between 3400 and 2900 Å present in the normal flame are not evident in the low temperature flame.¹⁰ The flame of carbon disulphide is strongly actinic.

Carbon disulphide vapour mixed with hydrogen and directed on to heated platinum reacts to form carbon and hydrogen sulphide.¹¹ Carbon disulphide inflames in the cold in contact with fluorine, and under varying conditions it reacts with chlorine, bromine and iodine.

¹ Carpmael, *British Patent*, 301561 (1927).

² Herz, *Ber.*, 1898, 31, 2669.

³ Bruhat and Pauthenier, *Compt. rend.*, 1924, 178, 1536; 179, 153; *Ann. Physique*, 1926, [x.], 5, 440.

⁴ Dixon and Russell, *Trans. Chem. Soc.*, 1899, 75, 612.

⁵ Sidot, *Compt. rend.*, 1872, 74, 179; 1875, 81, 32.

⁶ Berthelot, *ibid.*, 1898, 126, 1060.

⁷ Baker, *Phil. Trans.*, 1888, 179, 582.

⁸ Dixon and Russell, *Trans. Chem. Soc.*, 1899, 75, 612; Dixon and Higgins, *Mem. Manchester Lit. Phil. Soc.*, 1924-25, 69, 19.

⁹ See White, *J. Chem. Soc.*, 1927, p. 793. For the phosphorescent flame of carbon disulphide-methane mixtures in air or oxygen, and the influence of other gases, see Dixon and Higgins, *loc. cit.*

¹⁰ Emeléus, *J. Chem. Soc.*, 1926, p. 2948.

¹¹ Cossa, *Ber.*, 1868, 1, 117.

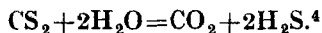
The production of thiophen when acetylene interacts with sulphur vapour has already been mentioned (p. 258). That this product is not the result of a secondary reaction between acetylene and carbon disulphide follows from the fact that thiophen is only produced in quantity from these two reactants at a considerably higher temperature than that required when sulphur is used. Acetylene saturated with carbon disulphide vapour and passed through an electrically heated tube containing broken porous pot, yields a condensate which at the optimum temperature of 700°C . contains about 10 per cent. by volume of thiophen and 10 per cent. of hydrocarbons.¹

Carbon disulphide readily undergoes oxidation and reduction (see p. 264). With alkalis it reacts to form a series of thio- or sulpho-salts (see p. 266 *et seq.*).

Hypochlorite solution converts carbon disulphide into carbonate and sulphate,² thus :



In the absence of alkali, oxidation, as for instance by permanganate solution, bromine water, or nitric or iodic acid, involves the separation of sulphur.³ Water and aqueous alkalis hydrolyse carbon disulphide at 150°C ., thus :



Heated with baryta water in an atmosphere of nitrogen, carbon disulphide yields barium hydrosulphide, which is subsequently converted into sulphate by contact with the air (see p. 264) :⁵



In alcohol solution, potassium hydroxide forms the xanthate (see p. 268).

Carbon disulphide interacts with dry ammonia, but the reaction has not yet been fully investigated ; the gas is slowly absorbed and a dark brown liquid results, which probably contains ammonium thiocarbonate and thiocyanate.⁶ An alcohol solution of ammonia readily dissolves carbon disulphide,⁷ the foregoing products being formed (see also p. 264).⁸

Carbon disulphide reacts additively with primary and secondary aliphatic amines to form alkylammonium salts of alkyldithiocarbamic acids. The products obtained with dimethylamine, diethylamine and piperidine, also certain derivatives of these products, are manufactured on a large scale for use as accelerators in the vulcanisation of rubber. With aromatic amines the disulphide reacts with elimination of hydrogen sulphide and formation of substituted thio-ureas, *e.g.* thiocarbanilide.

¹ Briscoe, Peel and Robinson, *J. Chem. Soc.*, 1928, p. 2857.

² Ritsema, *Chem. Zentr.*, 1904, ii., 1495.

³ Cloëz and Guinet, *Compt. rend.*, 1858, 46, 1110.

⁴ Schlagdenhauffen, *J. Pharm. Chim.*, 1856, [iii.], 29, 401.

⁵ Chancel and Parmentier, *Compt. rend.*, 1884, 99, 802.

⁶ Zeise, *Schweigger's J.*, 1822, 36, 1 ; 1824, 41, 98, 170 ; 1825, 43, 160 ; Berzelius and Marcet, *ibid.*, 1813, 9, 284 ; *Gilbert's Annalen*, 1814, 48, 157.

⁷ Zeise, *loc. cit.*

⁸ For the effect of heat on a mixture of carbon disulphide and ammonium carbonate, see Inghilleri, *Gazzetta*, 1909, 39, i., 634.

Carbon disulphide also combines with tertiary amines¹ and phosphines, forming crystalline substances, the most important of which is a scarlet compound with triethylphosphine, $\text{CS}_2 \cdot \text{P}(\text{C}_2\text{H}_5)_3$, to which the constitution $\text{CS}-\text{P}(\text{C}_2\text{H}_5)_3$ is attributed.² This substance is formed



immediately the reactants meet, and may be used to detect carbon disulphide in coal gas.

The Detection and Estimation of Carbon Disulphide.—Carbon disulphide may be detected by means of the red, crystalline compound which it forms with triethylphosphine³ and the white compound with phenylhydrazine.⁴ Minute quantities can also be detected by producing one of the dithiotrimercuric salts of the type $\text{HgX}_2 \cdot 2\text{HgS}$, which form characteristic crystalline precipitates when dilute aqueous solutions of mercuric salts are heated on a water-bath with carbon disulphide.⁵

Determination of the specific gravity of benzene before and after extraction of carbon disulphide with alcoholic potash gives a fairly accurate estimation of the quantity of carbon disulphide present, the error being less than 0.03 per cent. The following table shows experimental results obtained on shaking benzene containing 0.4 per cent. by volume of carbon disulphide for two hours with alcoholic potash (10 per cent.) containing varying concentrations of alcohol.⁶

	Per cent. Alcohol by Volume.	Vol. of Benzene. Vol. of Alcoholic Potash.	Sp. Gr. of Benzene + 0.4 per cent. CS_2 .	Sp. Gr. after Treatment.	Sp. Gr. when free from CS_2 .	Per cent. CS_2 in Total Mixture.
1	96.1	2	0.8861	0.8844	0.8844	0.45
2	89.6	2	0.8861	0.8845	0.8844	0.4
3	85.6	2	0.8861	0.8845	0.8844	0.4
4	77.5	2	0.8861	0.8845	0.8844	0.4
5	69.6	2	0.8861	0.8846	0.8844	0.4
6	49.8	2	0.8862	0.8848	0.8844	0.35
7	35.8	2	0.8862	0.8852	0.8844	0.25

Oxidation of the alkaline extract with bromine and subsequent estimation of the resulting sulphate also yields trustworthy results.⁶

Estimation of carbon disulphide by solution in alcoholic potash, with formation of the xanthate, followed by titration with standard copper sulphate, iodine, or permanganate solution which oxidises the xanthate to sulphate, according to Spielmann and Jones⁶ yields less trustworthy results.⁷

¹ Blennard, *Compt. rend.*, 1878, 87, 1040.

² Hofmann, *Annalen Suppl.*, 1861, 1., 26, 59; *Ber.*, 1880, 13, 1732.

³ Hofmann, *loc. cit.* The formation of this compound may also be made use of in the quantitative determination of the disulphide; see Hegel, *Zeitsch angew. Chem.*, 1926, 39, 431.

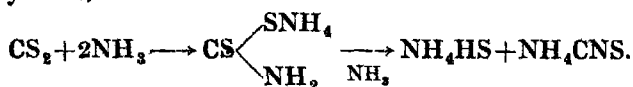
⁴ Fischer, *Annalen*, 1877, 190, 114; Liebermann and Seyewetz, *Ber.*, 1891, 24, 788; Busch, *ibid.*, 1894, 27, 2507.

⁵ Denigès, *Bull. Soc. chim.*, 1915, [iv.], 17, 353, 359.

⁶ Spielmann and Jones, *J. Soc. Chem. Ind.*, 1919, 38, 185 T.

⁷ See, however, Huff, *J. Amer. Chem. Soc.*, 1926, 48, 81; Harding and Doran, *ibid.*, 1907, 29, 1476; Macagno, *Gazzetta*, 1880, 10, 485; Schmitz-Dumont, *Chem. Zeit.*, 1897, 21, 487.

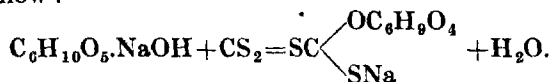
A further method for the estimation of carbon disulphide depends upon the fact that when heated with alcoholic ammonia at 60° C. under pressure, the disulphide is converted into a mixture of hydrosulphide and thiocyanate, thus :



The hydrosulphide may then be titrated with ammoniacal zinc solution ¹ (cf. p. 262).

Carbon disulphide may be estimated gravimetrically by treatment with baryta water (see p. 262), whereby barium sulphide is produced, which is then oxidised and weighed as sulphate.²

Uses and Physiological Properties of Carbon Disulphide.—Besides its employment as a solvent (see p. 260), carbon disulphide is used extensively in the manufacture of viscose silk. Viscose is a solution of the sodium salt of the cellulose ester of thiolthioncarbonic acid (p. 268) in water or dilute aqueous sodium hydroxide, or it may be described as an aqueous solution of the sodium salt of cellulose xanthic acid. For its production cellulose is steeped in concentrated sodium hydroxide solution and then pressed, the product being called alkali-cellulose and the formula $\text{C}_6\text{H}_{10}\text{O}_5\text{NaOH}$ assigned to it. This is converted into viscose by treatment with carbon disulphide, when the colour changes to golden yellow :



This product, after keeping for four or five days, is pressed through a "rose" perforated with small holes into a coagulating bath containing, for example, aqueous sulphuric acid (10 per cent.), when hydrated cellulose is precipitated in solid threads, which after purification and washing constitute viscose silk.

Much carbon disulphide is used in the rubber industry, particularly as a solvent for sulphur chloride in vulcanisation by the "cold" process or "vapour" process. It is also employed in the manufacture of numerous organic compounds used for the acceleration of vulcanisation, for example thiocarbamilide, alkyl xanthates (particularly zinc alkyl xanthates) and substituted dithiocarbamates (see p. 262). Many other compounds, such as ammonium thiocyanate and certain organic dyes containing sulphur, also require the use of carbon disulphide in their preparation.

The disulphide is used as an insecticide.

Carbon disulphide has a powerful toxic effect, producing headache, sickness, giddiness, a general weakening of the senses and muscular forces, and finally death.

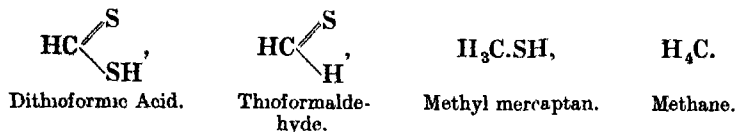
Reduction Products of Carbon Disulphide.

Just as by the reducing action of hydrogen on carbon dioxide formic acid, formaldehyde, methyl alcohol and methane may be directly or

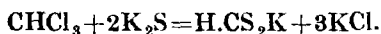
¹ Goldberg, *Zeitsch. angew. Chem.*, 1899, 12, 75.

² Chancel and Parmentier, *Compt. rend.*, 1884, 99, 892. See also Fisher (*Ind. Eng. Chem.*, 1927, 19, 1201) for a method involving oxidation to sulphate by means of alcoholic potash and hydrogen peroxide.

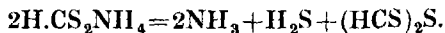
indirectly obtained, so from the analogous disulphide the following products should result :



Dithioformic Acid has been obtained ¹ by the addition of dilute hydrochloric acid to an alcohol solution of the potassium salt (see the following) cooled in ice. It separates as a white solid and there is a slight evolution of hydrogen sulphide during the reaction. The precipitate after filtering is washed with alcohol and ether. It is insoluble in the common solvents. On heating it melts at 55° to 60° C. with partial decomposition, which proceeds further at higher temperatures, the products being hydrogen sulphide, carbon disulphide, carbon and sulphur. *Potassium dithioformate* is obtained by treating chloroform with potassium sulphide in alcohol solution :



It forms golden-yellow crystals which melt to a red liquid at 198° C., undergoing decomposition as in the case of the free acid. *Ammonium dithioformate* cannot be obtained from chloroform and the sulphide, but it is formed on titration of the acid with ammonia. It decomposes on keeping, thus :



The *monosulphide* produced by this decomposition is also formed by the interaction of the potassium salt with cyanogen bromide :

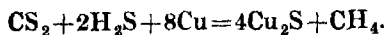


A *disulphide*, $[(\text{HCS})_2\text{S}_2]_x$, is formed as a yellowish-red precipitate when potassium dithioformate in alcohol solution is cautiously oxidised by the addition of iodine. It decomposes similarly to the acid above 200° C. Both sulphides are insoluble in the common solvents. Dithioformates of silver, lead, zinc and cobalt have also been described.²

From molecular weight determinations by cryoscopic methods, the esters of dithioformic acid appear to have a trimeric constitution, for example, $(\text{H.CS}_2\text{Me})_3$, and it is suggested ³ that the molecule of the acid is similarly constituted and possesses a cyclic structure with alternating carbon and sulphur atoms.

Thioformaldehyde, $(\text{H}_2\text{CS})_3$, results from the reduction of carbon disulphide by nascent hydrogen.⁴

Methyl mercaptan cannot be obtained directly from carbon disulphide, but *methane* may be prepared by passing the vapour together with hydrogen sulphide over heated copper :



¹ Levi, *Atti R. Accad. Lincei*, 1929, [vi.], 9, 170.

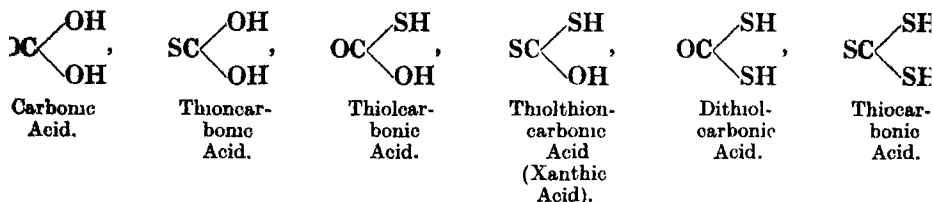
² Levi, *ibid.*, 1923, [v.], 32, i., 569.

³ Levi, *ibid.*, 1929, [vi.], 9, 170.

⁴ Girard, *Compt. rend.*, 1856, 43, 396.

Thio-acids and Salts Derived from Carbon Disulphide.

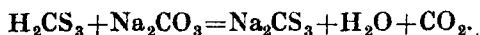
Carbon disulphide, like the dioxide, is the anhydride (or, more strictly, thioanhydride) of a feeble acid, thiocarbonic acid, H_2CS_2 . Moreover, between carbonic and thiocarbonic acids a number of intermediate acids are capable of existence. They are as follows :



Thiocarbonic Acid, H_2CS_2 .—Carbon disulphide reacts with soluble sulphides and the salts produced are the sulphur analogues of the carbonates. It was discovered by Berzelius that when carbon disulphide is brought into contact with sodium sulphide solution, the former dissolves, producing a solution from which alcohol precipitates sodium thiocarbonate, Na_2CS_3 , as a yellowish-brown oil. By the action of dilute hydrochloric acid on this salt thiocarbonic acid may be obtained as a reddish-yellow oil which possesses a very disagreeable odour¹ and is decomposed by heat into carbon disulphide and hydrogen sulphide, no free sulphur being formed.

Pure thiocarbonic acid is better obtained² by dropping pure solid ammonium thiocarbonate into a large excess of concentrated hydrochloric acid, when it separates as a bright red liquid which can be dried over phosphorus pentoxide. The liquid has a density of 1.47 at 17° C. and a surface tension at 12.5° C. of 48.3 dynes/cm.; it freezes to an orange-coloured solid at -30.5° C. The acid decomposes on keeping, giving carbon disulphide, in which it dissolves. It dissolves slightly in water, acids and many organic solvents, giving yellow solutions which gradually decompose with loss of colour. In acetone the decomposition is not accompanied by separation of sulphur even on long standing (*cf.* perthiocarbonic acid, p. 269).

Calcium and sodium carbonates react with the acid forming the corresponding thiocarbonates, thus :



An investigation of the freezing curve for the system CS_2 - H_2S has demonstrated the existence of two *thiohydrates*, $\text{CS}_2 \cdot \text{H}_2\text{S}$ and $\text{CS}_2 \cdot 6\text{H}_2\text{S}$, the former being isomeric with thiocarbonic acid.³

Ammonium thiocarbonate, $(\text{NH}_4)_2\text{CS}_3$. may be prepared by digesting ammonium pentasulphide with carbon disulphide under a reflux condenser; a white deposit of ammonium monosulphide first forms on the condensing surface and is gradually converted into the thiocarbonate, becoming pale orange-coloured. On exposure to moist air it turns red.

The thiocarbonates of the alkali and alkaline earth metals may also

¹ O'Donoghue and Kahan, *Trans. Chem. Soc.*, 1906, 89, 1812.

² Mills and Robinson, *J. Chem. Soc.*, 1928, p. 2326.

³ Biltz and Brautigam, *Zeitsch. anorg. Chem.*, 1927, 162, 49.

be obtained by the action of carbon disulphide on the corresponding hydroxides under certain conditions. On shaking carbon disulphide with aqueous sodium hydroxide, a deep red solution is obtained, the reaction being facilitated by warming to 80° C., and especially by the presence of emulsifying agents. The solution contains sodium trithiocarbonate sufficient in amount to satisfy the equation : ¹



No dithiocarbonate is formed, nor in freshly prepared solutions are polysulphides or thiosulphates present. With oxidising agents such as hydrogen peroxide or chlorine, the red solution yields sulphates, whilst salts of the heavy metals give coloured precipitates which are unstable when moist, decomposing to carbon disulphide and the metal sulphide.

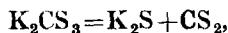
It was generally supposed that the removal of carbon disulphide from crude coal gas when purified by lime was due to its absorption by calcium sulphide with the formation of calcium thiocarbonate, but Yeoman ² suggests that it is the perthiocarbonate, CaCS_4 , which is formed. This suggestion accounts for the necessity of the presence of some oxygen in order that absorption may take place.

The thiocarbonates of the alkali and alkaline earth metals are soluble in water. The alkali thiocarbonates are yellow in colour. In concentrated solution these salts are fairly stable, but in dilute solution they are gradually decomposed, forming the carbonate and hydrogen sulphide.

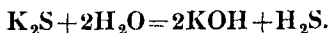
Under certain conditions thiocarbonates behave like simple sulphides ; thus, benzoyl chloride and a thiocarbonate in equimolecular proportions yield benzoyl disulphide, which substance is also formed by the interaction of benzoyl chloride and potassium hydrogen sulphide followed by oxidation. The complex salts of the thiocarbonates are more stable than the simple salts.

Thiocarbonates, especially the alkali thiocarbonates, are used in agriculture to prevent certain diseases, notably phylloxera of the vine. It is carbon disulphide which is the active material of these fungicides.³

It has been shown ⁴ that when a solution of potassium thiocarbonate is boiled in an atmosphere of nitrogen, the following change takes place :—



the sulphide subsequently undergoing hydrolysis, thus :



In the presence of air or oxygen, however, the reaction is as follows :—



¹ Weeldenburg, *Rec. Trav. chim.*, 1928, 47, 496.

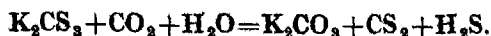
² Yeoman, *Trans. Chem. Soc.*, 1921, 119, 38.

³ For descriptions of various thiocarbonates, see O'Donoghue and Kahan, *loc. cit.*; Hofmann and Höchtlén, *Ber.*, 1903, 36, 1146; Holmberg, *J. prakt. Chem.*, 1906, [n.], 73, 239. See also Yeoman (*Trans. Chem. Soc.*, 1921, 119, 38) for details regarding the trithiocarbonates and the perthiocarbonates of the alkali and alkaline earth metals. For the preparation of alkyl and aryl trithiocarbonates from carbon disulphide, see Wertheim, *J. Amer. Chem. Soc.*, 1926, 48, 826. For data regarding the absorption spectra, etc., of thiocarbonic and perthiocarbonic acids, see von Valban, Mackert and Ott, *Zeitsch. Elektrochem.*, 1923, 29, 445.

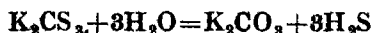
⁴ Tarugi and Magri, *Gazzetta*, 1909, 39, i., 405.

SULPHUR, SELENIUM, AND TELLURIUM.

and in an atmosphere of carbon dioxide :



It is believed that the reaction



cannot take place.

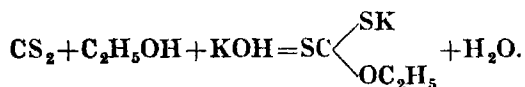
When carbon disulphide is heated with sodium alone in a sealed tube at 150° C., no reaction other than slight superficial tarnishing of the metal occurs; with a sodium-potassium alloy yellowish-brown explosive crusts are formed. When the liquid is shaken with sodium amalgam (0.8 per cent. Na) and the mixture then treated with 90 per cent. alcohol, a solution containing a complex mixture of compounds is obtained,¹ from which by treatment with methyl chloride the following compounds may be isolated: methyl sulphide, two isomeric methyl tetrathio-oxalates, methyl methylxanthate, tetramethylthioethylene and methyl trithiocarbonate (b.pt. 224° C. at 760 mm.). Similar products (except the xanthate) may be obtained by allowing carbon disulphide to react with sodium in solution in liquid ammonia and treating the resulting brown mass with methyl sulphate.

Salts and esters of the intermediate thio-acids are known, being prepared from carbon disulphide or carbon oxysulphide.

Thiolcarbonic Acid, HS.CO.OH, yields carbon oxysulphide, COS, by decomposition; its esters yield alcohols or mercaptans when saponified, according to whether the alkyl group is attached to oxygen or to sulphur; by this means the constitutions of the thiocarbonic acids are established.

It may be observed that thion- and thiol-carbonic acids are isomeric, as well as thiolthion- and dithiol-carbonic acids.

Xanthic Acid or **Xanthogenic Acid** is ethylthiolthioncarbonic acid. Its *potassium salt*, which is yellow and has a disagreeable smell, is prepared by the action of alcoholic potash on carbon disulphide :

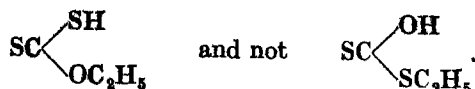


Analogous compounds are known containing other organic alkyl radicals in place of the ethyl radical.

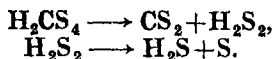
Xanthates are used commercially as flotation agents in "froth flotation" processes for the separation of crushed materials, and their use as vulcanisation accelerators for rubber has already been mentioned (p. 264).

Xanthic acid is obtained as a colourless oil by the action of dilute sulphuric acid on the potassium salt in the cold. It decomposes at 24° C. into ethyl alcohol and carbon disulphide. The ethyl ester, when heated with water, yields carbon dioxide, hydrogen sulphide, ethyl alcohol and ethyl mercaptan, whilst with ammonia, ethyl mercaptan and *xanthogenamide* or *thiourethane*, $C_2H_5O.CS.NH_2$, are produced. These reactions indicate that the constitution of the acid is

¹ Fetkenheuer and others, *Ber.*, 1927, 60, [B], 2528.



Perthiocarbonic Acid, H_2CS_4 .—This acid has not been obtained in a perfectly pure condition, but a dark brown liquid consisting largely of perthiocarbonic acid is obtained when the ammonium salt is treated with 98 per cent. formic acid.¹ The liquid is rapidly decomposed by acetone (*cf.* p. 266), the action being accompanied by crackling, the colour disappearing and sulphur being deposited :



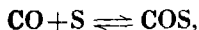
When the liquid is distilled under reduced pressure, using a small fractionating column, carbon disulphide is first obtained, followed at 70° C. by hydrogen disulphide, leaving a large residue of sulphur.

If concentrated hydrochloric acid is used instead of formic acid in the foregoing preparation, the resulting red liquid consists of a solution of sulphur in trithiocarbonic acid which dissolves quietly in acetone to give a yellow solution, the dissolved sulphur then gradually precipitating out.

Sodium perthiocarbonate, Na_2CS_4 , is formed when an alcoholic solution of sodium sulphide is converted into the disulphide by the addition of sulphur and subsequently treated with carbon disulphide.² Perthiocarbonates may also be formed by the direct combination of thiocarbonates with sulphur.³ There is no analogy to this latter method of preparation in the case of percarbonates ; this fact is usually regarded as illustrating the superior chain-forming power of sulphur atoms as compared with oxygen atoms.

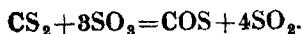
The *ammonium salt* may be obtained by extracting ammonium pentasulphide with carbon disulphide in a Soxhlet apparatus, washing first with hot carbon disulphide and then with ether, and centrifuging.⁴

Carbonyl Sulphide or Carbon Oxysulphide, COS .—Carbonyl sulphide, discovered by Than,⁵ is formed synthetically when a mixture of sulphur vapour and carbon monoxide is passed through a hot tube. The action is reversible,



so that the proportion of carbonyl sulphide formed depends upon the temperature and rate of passage of the gaseous mixture. Attempts to synthesise carbonyl sulphide by means of the electric spark seem to give negative results.⁶

Carbonyl sulphide is also formed by the interaction of carbon disulphide and sulphur trioxide, thus :



When sulphur vapour and air are passed over a red-hot mixture of

¹ Mills and Robinson, *J. Chem. Soc.*, 1928, p. 2326.

² Yeoman, *Trans. Chem. Soc.*, 1921, 119, 38.

³ Gélis, *Compt. rend.*, 1875, 81, 282.

⁴ Mills and Robinson, *loc. cit.*

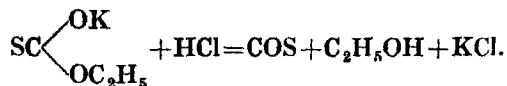
⁵ Than, *Annalen Suppl.*, 1867, 5, 236.

⁶ González and Moles, *Anal. Fis. Quim.*, 1919, 17, 55.

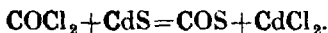
clay and carbon, and also when sulphur dioxide is passed over red-hot carbon, carbonyl sulphide is formed : ¹



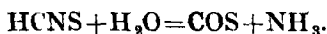
Some thiocarbonates yield carbonyl sulphide on decomposition, thus : ²



At 270° C. carbonyl chloride and cadmium sulphide interact according to the equation :



An important method of preparing carbonyl sulphide consists in the decomposition of a thiocyanate with moderately concentrated (14*N*) sulphuric acid, the liberated thiocyanic acid being hydrolysed thus :



The carbonyl sulphide is evolved at 20° C. together with hydrocyanic acid, formic acid and carbon disulphide. The gas is purified by passing through concentrated aqueous caustic potash to absorb the acid vapours, and the carbon disulphide is absorbed in a mixture of triethylphosphine, pyridine and nitrobenzene. After drying with sulphuric acid, the gas may be further purified by liquefaction or absorption in toluene.³

Carbonyl sulphide may also be obtained by the action of hydrochloric acid on commercial ammonium thiocarbamate, according to the equation :



In this case the gas may be purified by bubbling through 33 per cent. caustic soda solution in order to absorb carbon dioxide and hydrogen sulphide and dried with calcium chloride and phosphorus pentoxide. It is then condensed by means of liquid air, and finally fractionated.

Properties.—Pure carbonyl sulphide is a colourless, odourless gas, which is slowly decomposed by water. When dry it is stable, even in sunlight, and if kept over sulphuric acid it undergoes only slight decomposition. Its density at -87° C. is 1.24. It melts at -138.2° C. and boils at -50.2° C. under a pressure of 760 mm.⁴

1	volume of water	dissolves	0.54	volumes of COS	at 20° C.
1	"	"	alcohol	"	8.0 " " 22° C.
1	"	"	toluene	"	15.0 " " 22° C.

The thermal decomposition of carbonyl sulphide has been investigated.⁵ The products of dissociation may be carbon monoxide and

¹ Gautier, *Compt. rend.*, 1888, 107, 911; Berthelot, *ibid.*, 1883, 96, 298.

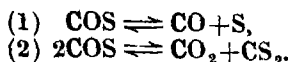
² Salomon, *J. prakt. Chem.*, 1872, 5, 476.

³ Klason, *ibid.*, 1887, [2], 36, 64; Hofmann, *Annalen Suppl.*, 1861-62, 1, 26, 59; Hempel, *Zeitsch. angew. Chem.*, 1901, 14, 865.

⁴ Stock and Kuss, *Ber.*, 1919, 50, 159.

⁵ Stock and Seelig, *ibid.*, 1919, 52, [B], 681; Stock, Siecke and Pohland, *ibid.*, 1924, 57, [B], 719.

sulphur on the one hand, or carbon dioxide and carbon disulphide on the other :



At 800° C. reaction (2) appears to proceed slowly in either direction, while (1) is very rapid. The fact that the degree of dissociation in (1) is independent of the amounts of carbon dioxide and carbon disulphide present, shows that carbon monoxide and sulphur are primary products of the decomposition of carbonyl sulphide and are not formed secondarily from the carbon dioxide and carbon disulphide. At temperatures below 400° C. decomposition according to equation (1) is not evident, while at 900° C. it reaches a maximum (64 per cent.); reaction (2) reaches a maximum at about 600° C., at which point 43 per cent. of the carbonyl sulphide is decomposed in this way and 16 per cent. according to reaction (1). The carbon monoxide equilibrium depends upon the pressure, whilst the carbon dioxide equilibrium does not. Nearly all the reactions involved in the thermal decomposition of carbonyl sulphide depend greatly on catalytic influences. Quartz is a pronounced catalyst for reaction (2), but has little influence on reaction (1). Carbonyl sulphide is comparatively rapidly decomposed in quartz vessels, but is stable when kept in glass apparatus. The viscosity of gaseous carbonyl sulphide is as follows : ¹

$$\eta_{15} = 1.200 \times 10^{-4} \text{ C.G.S. units,}$$

and

$$\eta_{100} = 1.554 \times 10^{-4} \text{ C.G.S. units ;}$$

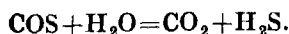
by extrapolation from Sutherland's formula, $\eta_0 = 1.135 \times 10^{-4}$ C.G.S. units. The mean area (\bar{A}) which the molecule presents in mutual collision is $1.06 \times 10^{-15} \text{ cm.}^2$.

The physiological effects of carbonyl sulphide are very similar to those of nitrous oxide.

When the pure gas is passed through a saturated solution of barium hydroxide or copper sulphate, no opalescence or precipitate is produced for at least half a minute ; if any carbon dioxide is present, however, the solution becomes milky at once. According to Weeldenburg ² there is no reaction between carbonyl sulphide and copper sulphate in neutral or acid solution, nor is there any reaction with iodine or ethereal triethylphosphine (*cf.* CS_2 , p. 263).

Carbonyl sulphide burns with a blue flame, forming carbon dioxide and sulphur dioxide. With air it forms a mixture which is slightly explosive except when quite dry.³ The explosive limits lie between 11.9 and 28.5 per cent. of carbonyl sulphide.⁴ A white-hot platinum wire completely decomposes the sulphide into carbon monoxide and sulphur.

Water slowly decomposes carbonyl sulphide, forming carbon dioxide and hydrogen sulphide :



¹ Smith, *Phil. Mag.*, 1922, [vi.], 44, 289.

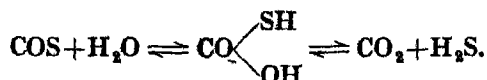
² Weeldenburg, *Rec. Trav. chim.*, 1928, 47, 496.

³ E. J. Russell, *Trans. Chem. Soc.*, 1900, 77, 361.

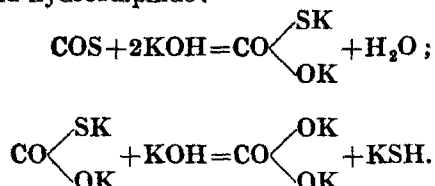
⁴ Hempel, *Zeitsch. angew. Chem.*, 1901, 14, 865.

172 SULPHUR, SELENIUM, AND TELLURIUM.

According to Buchböck¹ the reaction proceeds in two stages, thiol-carbonic acid being an intermediate product :

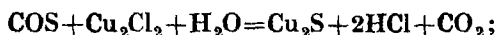


Aqueous solutions of the caustic alkalis act only slowly with the oxysulphide to form thiocarbonates, which, however, soon decompose into carbonate and hydrosulphide :

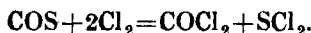


With alcoholic potash the reaction is more rapid.²

Heated mercury, copper, iron and silver remove sulphur from carbonyl sulphide ; cuprous chloride reacts according to the equation :



chlorine forms phosgene, COCl_2 , together with "sulphur dichloride" :



Halogen Derivatives of Sulphur and Carbon.

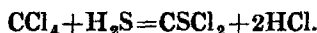
*Action of Chlorine on Carbon Disulphide.*³—Carbon disulphide is only slightly attacked by chlorine at ordinary temperatures, but in the presence of a chlorine carrier such as iodine, a reaction takes place with the ultimate formation of carbon tetrachloride. The following intermediate products have also been isolated :

- (1) Thiophosgene, CSCl_2 , b.pt. 73.5°C .
- (2) Trichloromethyl sulphur chloride or carbon tetrachlorosulphide, $\text{CCl}_3\text{.SCl}$, b.pt. 149°C .
- (3) Trichloromethyl disulphide, $\text{CCl}_3\text{.S}_2\text{.CCl}_3$, b.pt. 135°C . *in vacuo*.
- (4) Trichloromethyl trisulphide, $\text{CCl}_3\text{.S}_3\text{.CCl}_3$, a crystalline substance, m.pt. 57.4°C ., b.pt. 190°C . *in vacuo*.
- (5) Chlorothiocabonyl sulphur chloride, CSCl.SCl , b.pt. 140°C .

Thiocarbonyl Chloride, Carbon Dichlorosulphide, or Thiophosgene, CSCl_2 .—Thiocarbonyl chloride is produced by the prolonged action of dry chlorine on carbon disulphide :



or by passing mixed carbon tetrachloride and hydrogen sulphide vapours through a red-hot tube :⁴



¹ Buchböck, *Zeitsch. physikal. Chem.*, 1897, 23, 123 ; 1900, 77, 361.

² Bender, *Annalen*, 1868, 148, 138 ; Weeldenburg, *Rec. Trav. chim.*, 1928, 47, 496.

³ See Klason, *Ber.*, 1887, 20, 2376.

⁴ Kolbe, *Annalen*, 1843, 45, 41.

It may also be obtained by reduction of carbon tetrachlorosulphide, CSCl_4 , with tin and hydrochloric acid.¹

The chloride is a red, mobile liquid, with a suffocating odour. It has a density of 1.5085 at 15° C., and boils at 78.5° C. It fumes in moist air and is decomposed by water or alkalis, forming carbonic and hydrochloric acids or their salts and hydrogen sulphide.

Thiocarbonyl Tetrachloride, Carbon Tetrachlorosulphide, or Trichloromethyl Sulphur Chloride, CSCl_4 or $\text{Cl}_3\text{C.SCl}$.—Thiocarbonyl tetrachloride may be prepared by the action of dry chlorine on dried carbon disulphide in the presence of iodine.² It is a golden-yellow liquid, with an intensely disagreeable odour; it attacks the eyes and respiratory organs. Its density is 1.722.³ It boils at 149° C.⁴

When heated in a closed vessel to 200° C., thiocarbonyl tetrachloride decomposes with formation of sulphur chloride. It dissolves chlorine without being attacked. Water at 160° C. decomposes it entirely into carbon dioxide, hydrogen chloride and sulphur. It is also decomposed at ordinary temperatures by contact with metallic iron, the products being ferrous chloride and carbon tetrachloride,⁵ although according to de Fazi⁶ the reaction may, under special conditions, proceed according to the equation:



With certain catalysts a yield of 80 per cent. of thiocarbonyl chloride may be obtained.

Carbon Hexachlorosulphide or Trichloromethyl Trisulphide, $\text{C}_2\text{S}_3\text{Cl}_6$ or $\text{CCl}_3.\text{S}_3.\text{CCl}_3$.—This substance is present in the residue from the distillation of thiocarbonyl tetrachloride. It forms brilliant, colourless, prismatic crystals, which fuse at 57.4° C.⁷ and boil at 190° C. *in vacuo*.⁸

Trichloromethyl Disulphide, $(\text{CCl}_3\text{S})_2$ or $\text{CCl}_3.\text{S}_2.\text{CCl}_3$, may be obtained by the careful action of powdered silver on thiocarbonyl tetrachloride. It is a thick yellow oil, which boils at 135° C. *in vacuo*.⁹

Thiocarbonyl Sulphochloride or Chlorothiocarbonyl Sulphur Chloride, CS_2Cl_2 or CSCl.SCl , is a yellow oil, boiling at 140° C. *in vacuo*. It is obtained when carbon dichlorosulphide is heated with sulphur at 130° to 150° C. in a closed vessel.¹⁰

Carbon Bromosulphide, $\text{C}_2\text{S}_3\text{Br}_6$.—When a mixture of carbon disulphide and bromine is allowed to stand and is then distilled, a residue of composition CS_2Br_4 is obtained; this is decomposed by water or alcohol, forming sulphur bromide and carbon bromosulphide, $\text{C}_2\text{S}_3\text{Br}_6$. Carbon bromosulphide when heated gives rise to bromine, sulphur bromide, carbon tetrabromide and a blue substance of apparent composition $\text{C}_6\text{S}_4\text{Br}_4.2\text{H}_2\text{O}$.¹¹

¹ Frankland, Garner and Webster, *J. Soc. Chem. Ind.*, 1920, 39, 319. See also de Fazi, *Gazzetta*, 1924, 54, 251.

² Frankland, Challenger and Webster, *J. Soc. Chem. Ind.*, 1920, 39, 256, Klason, *loc. cit.*

³ Klason, *loc. cit.*; Rathke (*Annalen*, 1873, 167, 195) gives density 1.712.

⁴ Klason, *loc. cit.*

⁵ Frankland, Garner and Webster, *loc. cit.*

⁶ de Fazi, *Gazzetta*, 1923, 53, I., 175.

⁷ Rathke, *Annalen*, 1873, 167, 209.

⁸ Klason, *loc. cit.*

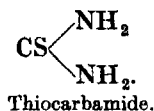
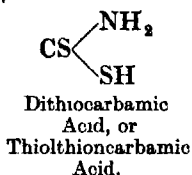
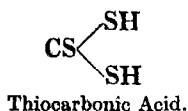
⁹ Klason, *loc. cit.*

¹⁰ Klason, *loc. cit.*

¹¹ Hell and Urech, *Ber.*, 1882, 15, 273; 1883, 16, 1144, 1147.

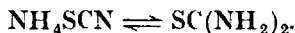
Amino-derivatives of Thiocarbonic Acid.

As carbamic acid and carbamide are related to carbonic acid, so are thiocarbamic acid and thiocarbamide related to thiocarbonic acid :

Dithiocarbamic Acid or Thiolthioncarbamic Acid, $\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{CS} \\ \diagdown \\ \text{SH} \end{array}$,

is obtained from its *ammonium salt*, which is formed by the combination of carbon disulphide with dry ammonia in the presence of alcohol, the salt crystallising in prisms.¹ Hydrochloric acid causes separation of the acid from an aqueous solution of the ammonium salt in the form of an unstable oil, which crystallises below 10° C., smells of hydrogen sulphide, is acid in reaction, and easily decomposes into hydrogen sulphide and thiocyanic acid.²

Thiocarbamide or **Thiourea**, $\text{CS}(\text{NH}_2)_2$, is formed by heating ammonium thiocyanate to 140° C., when it undergoes an intramolecular rearrangement :³



At the same time some *guanidine thiocyanate*, $\text{NH}:\text{C}(\text{NH}_2)_2\cdot\text{HSCN}$, is produced, although a larger proportion of this substance is formed at 170° to 180° C.⁴ The thiourea is freed from guanidine thiocyanate and unchanged ammonium thiocyanate by treatment with cold water, in which thiourea is but sparingly soluble; it may then be purified by recrystallisation from water.

Another method of preparation consists in heating carbon disulphide with ammonium carbonate in a sealed tube. The other product of this reaction is ammonium thiocyanate. The yield of thiocarbamide by this method is stated to be much below the theoretical value.⁵

Thiourea crystallises in rhombic prisms and is soluble in eleven times its weight of cold water. When heated with water to 140° C., ammonium thiocyanate is re-formed. It forms salts which are analogous to those of urea, the most characteristic being the nitrate, $\text{CS}(\text{NH}_2)_2\cdot\text{HNO}_3$. It is oxidised in solution containing blood charcoal according to the equation :



¹ For the formation of derivatives of the acid, see p. 262.

² Zeise, *Annalen*, 1843, 48, 95; Debus, *ibid.*, 1850, 73, 26; Mulder, *J. prakt. Chem.*, 1867, 101, 401; 1868, 103, 178.

³ Reynolds, *Trans. Chem. Soc.*, 1855, 8, 1.

⁴ Volhard, *Ber.*, 1874, 7, 92; *J. prakt. Chem.*, 1874, [ii.], 9, 6.

⁵ Gilfillan, *J. Amer. Chem. Soc.*, 1920, 42, 2072. For a study of the equilibrium between thiocarbamide and ammonium thiocyanate, see Burrows, *ibid.*, 1924, 46, 1623.

⁶ For the kinetics of this reaction, see Freundlich and Fischer, *Zeitsch. physikal. Chem.*, 1925, 114, 413.

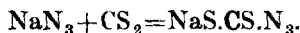
Thiourea is used with formaldehyde on a large scale for the production of synthetic resins. It can also be used to produce excellent mirrors of galena on glass.

Azidodithiocarbonic Acid, HS.CS.N_3 .—This acid has been prepared¹ by allowing sodium azide, NaN_3 , dissolved in a little water, to react with carbon disulphide; after keeping the mixture in a stoppered vessel at 40°C . for 48 hours, the resulting solution on treatment with concentrated hydrochloric acid at 0°C . yields a white or very pale yellow crystalline precipitate of the azido-acid. The crystals belong to the monoclinic system. The acid is fairly soluble in water, more soluble in organic solvents. It has the characteristic properties of a strong acid, and it is oxidised by various agents, yielding azido carbon disulphide, $(\text{S.CS.N}_3)_2$, some sulphate also being formed. At ordinary temperatures the acid undergoes spontaneous decomposition with formation of thiocyanic acid as an intermediate product,



the resulting solid product consists of a mixture of polymerised thiocyanic acid and free sulphur.

The alkali azidodithiocarbonates may be obtained by the action of carbon disulphide vapour on an aqueous solution of the alkali azide at 40°C .² With a 1 per cent. solution of sodium azide the action proceeds quantitatively:



If the SCSN_3 -group be considered as a unit, azidodithiocarbonic acid may be regarded as a halogenoid hydracid having the same relation to azido carbon disulphide as hydrogen chloride bears to chlorine,³ and undergoing ionisation in solution in accordance with:



Azido carbon disulphide, $(\text{S.CS.N}_3)_2$, may be prepared by the oxidation of the foregoing compound or its salts. It is a white, crystalline solid, very sparingly soluble in water. At ordinary temperatures it decomposes spontaneously, yielding nitrogen, sulphur and a polythiocyanogen:



It reacts with caustic potash in much the same manner as a halogen, forming the potassium salts of azidodithiocarbonic acid and azido-oxodithiocarbonic acid:



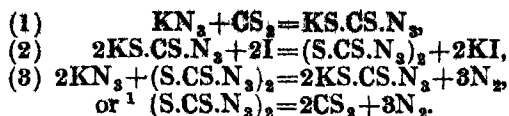
Potassium azide reacts with iodine in the presence of carbon disulphide to form potassium iodide and nitrogen as the final products, but the reaction appears to proceed according to the following scheme:⁴

¹ Smith and Wilcoxon, *J. Amer. Chem. Soc.*, 1923, 45, 2604.

² Currier and Browne, *ibid.*, 1922, 44, 2849; Browne and Hoel, *ibid.*, p. 2315.

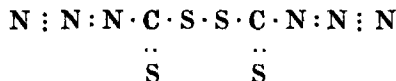
³ See Smith and Wilcoxon, *loc. cit.*; Browne, Hoel, Smith and Swezey, *ibid.*, 1923, 45, 2541.

⁴ Browne and Hoel, *ibid.*, 1922, 44, 2106.



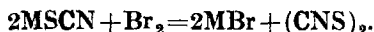
The reaction is facilitated by the presence of alcohol or acetone, and it may be used for the determination of azides. The catalytic effect of sulphides and thiosulphates on this reaction has already been mentioned (pp. 65, 205).

The following formula has been suggested for azido carbon disulphide : ²



Thiocyanogen and its Derivatives.

Thiocyanogen, (CNS)₂.—Thiocyanogen was first obtained by Söderbäck by the action of bromine or iodine on a suspension of the thiocyanate of silver, lead, cadmium, mercury, zinc, thallium or copper in carbon disulphide : ³

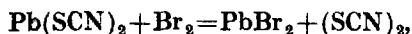


It may also be prepared by electrolysis of the alkali thiocyanates in aqueous or alcoholic solution, using a platinum gauze anode and a silver cathode. On evaporation under reduced pressure, thiocyanogen is obtained as a viscous oil, solidifying at -70°C .⁴

A usual method for the preparation of a solution of thiocyanogen is to treat lead thiocyanate with a dry ethereal solution of bromine cooled in ice.

When a solution of thiocyanogen in carbon disulphide is cooled to -70°C ., the thiocyanogen is obtained in cruciform aggregates of almost colourless crystals, melting at -2° to -3°C . On warming to ordinary temperatures the thiocyanogen becomes reddish-brown in colour and more viscous ; finally a brick-red amorphous solid is obtained. Thiocyanogen is very readily soluble in ethyl alcohol and ether, slowly soluble in carbon disulphide and carbon tetrachloride.⁵

In many of its reactions, and in its molecular formula, thiocyanogen shows a close analogy with the halogens. Its molecular weight has been determined by the cryoscopic method, allowing a known weight of bromine to react with lead thiocyanate in the presence of bromoform,



and measuring the depression of the freezing-point thus obtained. The result obtained is in agreement with that required by the molecular formula (CNS)₂.⁶

When thiocyanogen is treated with chlorides or bromides no appreciable effect is produced. It liberates iodine from aqueous or alcoholic

¹ Feigl and Chargaff, *Zeitsch. anal. Chem.*, 1928, 74, 376.

² Browne, Hoel, Smith and Swezey, *loc. cit.*

³ Söderbäck, *Annalen*, 1919, 419, 217.

⁴ Kerstein and Hoffmann, *Ber.*, 1924, 57, [B], 491.

⁵ Söderbäck, *loc. cit.*

⁶ Lecher and Goebel, *Ber.*, 1921, 54, [B], 2223.

solutions of the iodides of cadmium, lead, silver and mercury. When treated with iron powder, or mercury, the corresponding thiocyanates are formed. Water interacts with thiocyanogen to form thiocyanic acid, hydrogen cyanide and sulphuric acid.

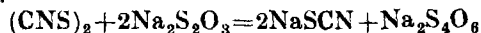
The reactions of thiocyanogen may roughly be divided into two types: (1) Reactions in which the radical combines directly with metals to form the corresponding thiocyanates, and with cuprous thiocyanate to form the cupric salt. (2) Reactions in which a substitution is effected; for example, with aniline, dimethylaniline and phenol, the corresponding *p*-thiocyano-derivatives and thiocyanic acid are formed.¹

According to Kerstein and Hoffmann² a further analogy between thiocyanogen and iodine lies in the formation of trithiocyanates (*cf.* tri-iodides) by the union of thiocyanogen with thiocyanates. These trithiocyanates behave like free thiocyanogen, except for their lesser sensitiveness towards water.

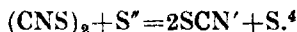
Thiocyanogen in solution in chloroform may react with chlorine in three distinct ways yielding (1) thiocyanogen monochloride, SCNCl , (2) sulphur chloride and cyanuric chloride, and (3) thiocyanogen trichloride, SCNCl_3 .³

Estimation of Thiocyanogen.—Solutions of thiocyanogen in organic solvents can be titrated accurately by agitation with at least twice the equivalent quantity of potassium iodide and determination of the liberated iodine.

The application of thiocyanogen in volumetric analysis is restricted by the necessity of using anhydrous solvents and dry vessels, to avoid hydrolysis. With a sufficient excess of sodium thiosulphate or hydrogen sulphide, respectively, thiocyanogen reacts quantitatively according to the equations:

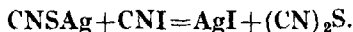


and



Cyanogen Monosulphide or Thiocyanic Thioanhydride $(\text{CN})_2\text{S}$.

—This compound is formed by the interaction of silver thiocyanate and cyanogen iodide in ether solution, silver iodide separating out:⁵



It is also formed when mercuric cyanide is treated with sulphur chloride, and together with cyanogen trisulphide, $(\text{CN})_2\text{S}_3$, when silver cyanide interacts with sulphur chloride.⁶

Cyanogen monosulphide crystallises in rhomboidal crystals which partly sublime at 30° C. and melt at 60° C. It is soluble in water, alcohol, ether, carbon disulphide, chloroform, benzene and sulphuric acid. It is decomposed by hydrochloric acid. It precipitates iodine from potassium iodide. Alcoholic potash decomposes it into potassium cyanate and potassium thiocyanate:



¹ Challenger, Smith and Paton, *Trans. Chem. Soc.*, 1923, 123, 1046.

² Kerstein and Hoffmann, *Ber.*, 1924, 57, [B], 491.

³ Kaufmann and Liepe, *ibid.*, 1924, 57, [B], 923.

⁴ Kaufmann and Gaertner, *ibid.*, 1924, 57, [B], 928.

⁵ Linnemann, *Annalen*, 1849, 70, 36.

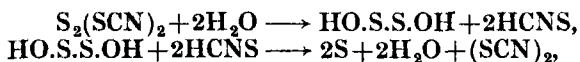
⁶ Schneider, *J. prakt. Chem.*, 1885, [2], 31, 197; 32, 187.

This is in accordance with its character as a thio-anhydride. It is transformed into hydrogen cyanide and thiocyanic acid by the action of hydrogen, hydrogen sulphide or potassium sulphide.

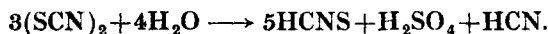
Cyanogen Trisulphide, $(\text{CN})_2\text{S}_3$ or $(\text{CN})_4\text{S}_6$.—The non-volatile residue which is formed when silver cyanide acts on sulphur chloride constitutes cyanogen trisulphide. It is a dark yellow crystalline powder, insoluble in water, alcohol, ether, carbon disulphide and chloroform. It is unattacked by hydrochloric acid and is soluble in concentrated sulphuric acid. It is transformed into carbon dioxide and sulphuric acid by nitric acid or aqua regia. When distilled, the products are carbon disulphide, sulphur and tricyanuramide, $\text{N}_3(\text{C}_3\text{N}_3)_3$.¹

Sulphur Thiocyanate, $\text{S}(\text{SCN})_2$, is formed as colourless, pearly crystals, when a solution of thiocyanogen in ether reacts with dry hydrogen sulphide. It decomposes at atmospheric temperatures. Heated in an open tube on a water-bath it darkens rapidly and then suddenly decomposes, evolving orange fumes. A solution of sulphur thiocyanate in a mixture of ether and benzene does not react with powdered iron, but on the addition of a drop of water the characteristic red colour of ferric thiocyanate develops immediately. By this reaction sulphur thiocyanate can be distinguished from free thiocyanogen.²

Disulphur Dithiocyanate, $\text{S}_2(\text{SCN})_2$, is formed³ by the interaction of sulphur chloride and a metallic thiocyanate, the best and most uniform results being obtained when mercuric thiocyanate is used. Chloroform or carbon tetrachloride forms a suitable solvent if the product is only required in solution, since these do not dissolve mercury salts; if the compound is to be isolated, carbon disulphide is the required solvent. Disulphur dithiocyanate forms colourless crystals which melt at -3.3°C ., forming a viscous, yellow, odourless liquid, which is somewhat unstable. On cautious heating it becomes dark yellow, then red, and finally detonates. It is hydrolysed by water according to the equations:



and



Thiocyanic Acid, Sulphocyanic Acid or Rhodanic Acid, HSCN .—This acid was isolated by Winterl (1790), Buchholz (1798) and Rink (1804).⁴ Its potassium salt was first prepared by Porret in 1808 by boiling potassium sulphide solution with Prussian blue. The composition of the acid was first determined by Berzelius in 1820.⁵ The question of the formation of the acid in animals has been the subject of investigation by Dezani and others, but their results have led to the conclusion that the acid is not produced in the animal organism, but is purely exogenetic.⁶

An aqueous solution of thiocyanic acid may be prepared by the decomposition of either silver or mercuric thiocyanate with hydrogen sulphide, or by decomposing barium thiocyanate with an equivalent quantity of sulphuric acid. It may also be obtained by distilling

¹ Schneider, *loc. cit.*; V. Meyer, *J. prakt. Chem.*, 1885, [2], 32, 210.

² Lecher and Wittwer, *Ber.*, 1922, 55, [B], 1481.

³ Lecher and Wittwer, *loc. cit.*

⁴ Rink, *Neues allgem. J. Chem. v. Gehlen*, 1803, 2, 460.

⁵ Berzelius, *Schweigger's J.*, 1820, 31, 42.

⁶ See Dezani, *Arch. Farm. Sperm.*, 1917, 23, 245; 24, 113; 1918, 26, 115; 1919, 28, 28.

potassium thiocyanate with a dilute acid such as sulphuric, phosphoric, oxalic or tartaric acid.¹

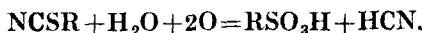
The acid may be obtained in the anhydrous state by distilling its potassium salt with dilute sulphuric or phosphoric acid, passing the vapour through a long calcium chloride tube and then condensing it in a freezing mixture. A better way is to drop concentrated sulphuric acid on to a mixture of potassium thiocyanate and phosphorus pentoxide in an atmosphere of hydrogen. The acid distils over under a pressure of 40 to 60 mm.² It is stated³ that still better results are obtained by this latter method if potassium hydrogen sulphate is used in place of sulphuric acid.

At ordinary temperatures thiocyanic acid is a clear, yellowish, volatile, oily liquid, of unknown boiling-point, which when sufficiently cooled forms colourless crystals, stable in dry hydrogen at -15°C ., melting at 5°C ., and readily decomposing with evolution of heat into hydrocyanic acid and *isoperthiocyanic acid*, $\text{C}_2\text{N}_2\text{S}_3\text{H}_2$. The vapour of thiocyanic acid is stable. The acid is readily soluble in water, alcohol, ether and benzene. It has a corrosive action on the skin. Hydrogen peroxide oxidises it according to the equation :



This reaction is accelerated by the presence of nickel and cobalt salts.⁴

Cryoscopic measurements on the acid in benzene, etc., indicate a mixture of single and double molecules. Single molecules of thiocyanic acid may be represented by the formula $\text{N}\equiv\text{C}-\text{SH}$ or $\text{S}:\text{C}=\text{NH}$. Probably the inorganic salts and the esters derived from them have the constitution represented by the first formula. The esters are converted into sulphonic acids and hydrocyanic acid by oxidation,



and are reduced by nascent hydrogen to mercaptans :



They can, however, undergo isomeric change into the esters of *iso*-thiocyanic acid, these esters constituting the mustard oils :



This change is accompanied by the evolution of heat, which for the methyl ester amounts to 6800 calories.⁵

Measurements of the molecular refraction of thiocyanates have been made.⁶

The heat of formation of thiocyanic acid in aqueous solution from its elements is $-19,900$ calories, and from $\text{HCN aq.} + 5800$ calories.⁷

¹ Beilstein and Geuther, *Annalen*, 1858, 108, 92.

² Rosenheim and Levy, *Ber.*, 1907, 40, 2166.

³ Rück and Steinmetz, *Zeitsch. anorg. Chem.*, 1912, 77, 51.

⁴ Kastle and Smith, *Amer. Chem. J.*, 1904, 32, 376. See also Rosenheim and Levy, *Ber.*, 1907, 40, 2166; Rück and Steinmetz, *loc. cit.*; Freundlich and Seal, *Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 257.

⁵ Thomsen, *Thermochemische Untersuchungen*, 1886, vol. iv. See Landolt-Bornstein, *Tabellen*, 4th ed. (Berlin, 1912), p. 849.

⁶ Dixon and Taylor, *Trans. Chem. Soc.*, 1910, 97, 927.

⁷ Joannes, *Compt. rend.*, 1882, 94, 797.

280. SULPHUR, SELENIUM, AND TELLURIUM.

An aqueous solution of thiocyanic acid is largely ionised and approaches hydrochloric acid in strength.

In the following table are given the conductivity (λ_v) and degree of dissociation (γ) at various dilutions (v litres) at 25° C., whence the constant K is calculated.¹

v .	λ_v .	γ .	K .
2	326	0.88346	4.74
4	337	0.91328	4.81
8	345	0.93495	4.75
16	352	0.95392	4.94
512	369	1.00000	..
			Mean=4.81

When an alkali thiocyanate is warmed with moderately concentrated sulphuric or hydrochloric acid, a yellow solid separates and carbonyl sulphide gas is evolved, which burns with a pale sulphurous flame. The yellow substance contains *isoperthiocyanic* acid, formed, together with hydrocyanic acid, according to the reaction :



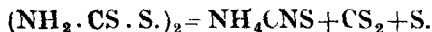
The carbonyl sulphide is produced, together with ammonia, by hydrolysis of the thiocyanic acid, which hydrolysis, according to Klason,² is preceded by the formation of thiolcarbamic acid, thus :



Besides these products there are others, including hydrogen sulphide and sulphur, which react with the thiocyanic acid to produce the disulphide of thiolthioncarbamic acid, thus :



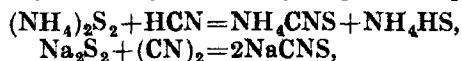
This compound, however, decomposes on warming, yielding ammonium thiocyanate, carbon disulphide and sulphur, thus :



Under the action of zinc and hydrochloric acid, thiocyanic acid is reduced to trithioformaldehyde, ammonia, methylamine, hydrogen sulphide and hydrocyanic acid.³ Bromine oxidises thiocyanates quantitatively in aqueous solution, thus :⁴



The Thiocyanates.—The salts of thiocyanic acid are generally obtained by the direct action of sulphur or a polysulphide on the cyanide, by the action of hydrogen cyanide or cyanogen on a polysulphide,



¹ Ostwald, *Lehrbuch der allgem. Chem.*, 1903, ii., 1, 729; Rudolph, *Zetsch. physikal. Chem.*, 1895, 17, 393.

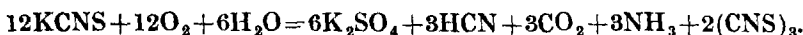
² Klason, *J. prakt. Chem.*, 1887, [ii.], 36, 57; 1888, 38, 383.

³ Hofmann, *Ber.*, 1867, 1, 179.

⁴ König, *J. prakt. Chem.*, 1911, [ii.], 84, 558.

or by the decomposition of a complex cyanide by fusion with an alkali carbonate and sulphur.¹

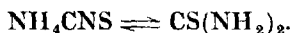
The thiocyanates are generally soluble in water, the exceptions being those of lead, silver, mercury and copper. Most of them dissolve also in alcohol and ether. Aqueous solutions of the alkali thiocyanates undergo atmospheric oxidation under the influence of sunlight; with solutions of medium concentration this change takes place rapidly, with separation of a yellow, amorphous precipitate consisting of *pseudo-cyanogen sulphide*, $(\text{CNS})_2$ (cf. p. 236). The concentration of thiocyanate most favourable to the separation of this sulphide is about 50 per cent. in summer and 10 per cent. in winter. In addition to this substance the products of the photochemical oxidation of potassium thiocyanate include hydrocyanic acid, sulphate, carbon dioxide, ammonia and ammonium salts:



An unstable intermediate peroxygenated compound is also always formed. This gives a blue coloration to fresh guaiacum tincture and is possibly analogous to Caro's acid.²

Any pink colour that may develop in solutions of alkali thiocyanates on exposure to light is due to oxidation of traces of ferrous salts usually present by dissolved oxygen.³

On heating, ammonium thiocyanate is converted into thiourea⁴ (see p. 274):



The existence of a compound of ammonium thiocyanate and thiourea, $\text{NH}_4\text{CNS} \cdot 4\text{CS}(\text{NH}_2)_2$, is indicated by the melting-point diagram.⁵ Ammonium thiocyanate forms a condensation product with formaldehyde, this being only sparingly soluble in water and ordinary solvents, and decomposed by strong acids or alkalis.⁶

The thiocyanates, except those of the heavy metals, are decomposed in the cold by dilute mineral acids, and on heating, the free thiocyanic acid distils over. With moderately concentrated acid, carbonyl sulphide is produced (see p. 270), whilst concentrated sulphuric acid causes rapid decomposition, with evolution of pungent vapours containing carbonyl sulphide, formic acid, carbon dioxide and sulphur dioxide.

The reaction between ferric salts and alkali thiocyanate, which constitutes the well-known test for ferric iron, has been the subject of much investigation.⁷ It may be represented simply thus,



¹ Loew, *J. prakt. Chem.*, 1853, 60, 478.

² Ganaasini, *Boll. Chim. farm.*, 1919, 58, 457.

³ See Montignie, *Bull. Soc. chim.*, 1928, [iv.], 43, 106; Patten and Smith, *Trans. Roy. Soc. Canada*, 1928, [iii.], 22, III, 221.

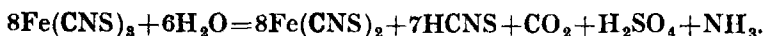
⁴ Reynolds and Werner, *Trans. Chem. Soc.*, 1903, 83, 1.

⁵ Smits and Kettner, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 683. See also Foote and Hunter, *J. Amer. Chem. Soc.*, 1920, 42, 69; 1921, 43, 1018, 1038.

⁶ Schmerda, *Zeitsch. angew. Chem.*, 1917, 30, 1, 176.

⁷ See Vol. IX., Part II., of this Series, p. 236. Also Bongiovanni, *Gazzetta*, 1907, 37, i., 472; 1908, 38, ii., 5, 299; *Boll. Chim. farm.*, 1910, 49, 789.

the resulting blood-red colour being said to be due to non-ionised ferric thiocyanate, its intensity depending on the product of the concentrations of ferric and thiocyanate ions. On dilution the solution becomes decolorised, possibly owing to hydrolysis of non-ionised thiocyanate into yellow colloidal ferric hydroxide and thiocyanic acid.¹ Philip and Bramley,² however, confirm the judgment of other observers that the loss of colour is associated with reduction of the iron, and they show that the following equation approximately represents the change in aqueous solution :



The discharging of the colour by oxalates, tartrates, etc., appears to be caused by the formation of complex ions with the ferric ions of the ionised ferric thiocyanate, which causes further dissociation of the red non-ionised salt and consequent loss of colour.

Ferric thiocyanate is readily soluble in aqueous ether, and the extract possesses a deep violet colour which can be completely discharged by the addition of ferric chloride. The explanation of this effect put forward by Clarens³ is that an excess of thiocyanate is necessary for the formation of ferric thiocyanate ; when a ferric salt is added this excess of thiocyanate is removed and a salt of dithiocyanic acid, insoluble in ether, is formed.⁴

Silver thiocyanate, formed as a white, flocculent precipitate by double decomposition, is insoluble in dilute mineral acids. It is upon the formation of this salt that Volhard's volumetric method for the determination of silver or of thiocyanate (see p. 283) depends.

Both cupric and cuprous thiocyanates may be obtained by precipitation. The former, which forms as a black precipitate when excess of thiocyanate is added to a copper salt, is unstable, and if allowed to remain under water, loses thiocyanic acid and forms the cuprous salt.⁵ The latter is precipitated as a white powder by the addition of a soluble thiocyanate to a solution of copper sulphate in the presence of sulphurous acid.

Mercuric thiocyanate, which is formed as a white precipitate when mercuric nitrate and potassium thiocyanate solutions are mixed, is soluble in excess of either solution. When dried, this salt is inflammable, forming a voluminous ash known as "Pharaoh's serpents." By the interaction of a mercuric salt with ammonium thiocyanate and thiocarbamide in acetic acid solution in the presence of an oxidising agent, or by the action of hydrogen sulphide on mercuric thiocyanate, the phototropic compound HS.Hg.CNS is obtained.⁶

The Detection and Estimation of Thiocyanates.—A thiocyanate may be detected by its behaviour with sulphuric acid (p. 281) and by the blood-red colour produced with ferric chloride, which colour is dis-

¹ Other views are put forward in Vol. IX., Part II., of this Series, p. 236. See Krüss and Moraht, *Ber.*, 1889, 22, 2054, 2061 ; *Zeitsch. anorg. Chem.*, 1892, 1, 399 ; Tarugi, *Gazzetta*, 1904, 34, ii., 326.

² Philip and Bramley, *Trans. Chem. Soc.*, 1913, 103, 795.

³ Clarens, *Bull. Soc. chim.*, 1923, [iv.], 33, 988.

⁴ See also Durand and Bailey, *ibid.*, p. 654 ; Brioni, *Gazzetta*, 1908, 38, ii., 638.

⁵ See Philip and Bramley, *Trans. Chem. Soc.*, 1916, 109, 97.

⁶ Venkataramaiah and Rao, *Nature*, 1923, 111, 775. For further description of the thiocyanates mentioned here and other metallic thiocyanates, see under the various metals in other volumes of this Series.

charged by mercuric chloride owing to the formation of the complex salt HgCNS.HgCl_2 , and by Rochelle salt owing to the formation of undissociated ferric tartrate. The red compound is soluble in ether. The reaction is extremely sensitive, but it cannot be applied to the colorimetric estimation of thiocyanates.¹

Evolution of nitrogen from sodium azide-iodine mixture is brought about by traces of thiocyanate, and the latter may readily be detected by this means in the presence of most inorganic oxy-acids and the common organic acids.² Sulphides and thiosulphates interfere (see pp. 65, 205) and must previously be removed by means of mercuric chloride.

Thiocyanates may be estimated gravimetrically by precipitation as cuprous thiocyanate, or in the absence of halogen acids and hydrocyanic acid, as silver thiocyanate. Other methods depend on oxidation to sulphate and precipitation with barium chloride. The oxidation may be brought about by means of bromine water³ or by a reagent, containing chlorine, prepared by electrolysis of a solution containing sodium and magnesium chlorides.⁴ The thiocyanate ion is also quantitatively precipitated as copper-pyridine thiocyanate, $[\text{CuPy}_2](\text{CNS})_2$, by the addition of a little pyridine and excess of cupric sulphate solution.⁵

Volumetrically, thiocyanate is estimated by Volhard's method, which involves titration with standard silver nitrate solution containing nitric acid, ferric alum being used as indicator. Cuprous thiocyanate dissolved in ammonium hydroxide solution and acidified with dilute sulphuric acid may be titrated with permanganate.⁶ An iodometric method has also been described.⁷

The Complex Thiocyanates.—The alkali thiocyanates show a marked tendency to form double and complex salts with the thiocyanates of other metals. The double salts in general resemble in type the double halides. Such compounds as $\text{KAg}(\text{CNS})_2$ and $\text{K}_2\text{Ag}(\text{CNS})_3$ may be considered as derivatives of di- and tri-thiocyanic acids, but in the salt $(\text{NH}_4)_5\text{Ag}(\text{CNS})_6$ the silver is not precipitated by the addition of chloride ion.⁸

The alkaline earth metals yield compounds of the type $\text{R}_2\text{M}(\text{CNS})_4$, where R is an alkali metal or silver; these are of interest since double halides of this type containing alkali and alkaline earth metals are not known.

Many compounds containing three metals, for example, of the types $\text{Cs}_2\text{Ag}_2\text{M}(\text{CNS})_6$, ($\text{M}=\text{Ca}, \text{Mg}, \text{Mn}$ or Cd), and $\text{CsMn}(\text{CNS})_6$, ($\text{M}=\text{Ag}_2$ or Cu), have also been prepared.⁹

Certain trivalent metals yield series of double thiocyanates which

¹ See Durand and Bailey, *Bull. Soc. chim.*, 1923, iv., 33, 654. For the sensitiveness of this reaction alone and in presence of iodide, acetate or nitrite, see Curtman and Harris, *J. Amer. Chem. Soc.*, 1916, 38, 2622.

² Feigl and others, *Mikrochem.*, 1929, 7, 10.

³ See also the use of nascent bromine, Treadwell and Mayr, *Zeitsch. anorg. Chem.*, 1915, 92, 127.

⁴ See Dubosc, *Ann. Chim. anal.*, 1921, 3, 297.

⁵ Spacu, *Bul. Soc. Stiinta Chy.*, 1922, i., 302.

⁶ Ronnet, *Ann. Chim. anal.*, 1911, 16, 336.

⁷ Schwicker, *ibid.*, 1929, 77, 278. For the detection and estimation of thiocyanates in the presence of ferrocyanides, see Perciabosco, *Annali Chim. Appl.*, 1923, 13, 346.

⁸ Cernatescu, *Bull. Acad. Sci. Roumanie*, 1920, 6, 53.

⁹ For a description of these and many other such compounds, see Wells and others, *Amer. Chem. J.*, 1902, 28, 245; 1903, 29, 474; 30, 144, 184; *Amer. J. Sci.*, 1922, [5], 4, 27; Bjerrum and Kirschner, *Det. K. Danske. Vidensk. Selsk. Skrifter. Nat. Math.*, 1915, 7, 76.

may be considered as salts of hypothetical acids of the type $H_3[M(CNS)_3]$; for example, iron,¹ chromium² and bismuth³ give such compounds.

Complex compounds of thiocyanates and arsenious oxide, for example $KCNS.2As_2O_3$ (microscopic hexagonal platelets), and an asbestos-like mass approximating in composition to $2NaOH.NaCNS.2As_2O_3.4H_2O$, have been prepared,⁴ as also have alkali and ammonium salts of thiocyanatocobaltous acid, $K_2Co(CNS)_4$ and $(NH_4)_2Co(CNS)_4$.⁵ By the action of ammonia on the latter salt, cobaltotetrammine thiocyanate, $Co(CNS)_2(NH_3)_4$, has been obtained as rose-red needles.⁶

Dithiocyanic Acid, $(HCNS)_2$, is obtained by decomposing its potassium salt with sulphuric acid. The potassium salt is formed when perthiocyanic acid (see below) is treated with a cold aqueous solution of potassium hydroxide.⁷ It is a dark yellow powder, slightly soluble in cold water, more soluble in hot water; it is soluble in alcohol and in ammonia. Aqueous and alcoholic solutions made in the cold do not colour ferric salts.⁸

Trithiocyanuric Acid, $(HCNS)_3$, may be obtained by treating cyanuric chloride with sodium sulphide.⁹ It forms yellow needles, stable up to $200^\circ C.$, soluble in water. At $200^\circ C.$ hydrochloric acid transforms it into cyanuric acid.

Perthiocyanic Acid, $H_2C_2N_2S_3$, may be prepared by the action of mineral acids on thiocyanic acid. When potassium thiocyanate (100 parts) dissolved in water (60 parts), and slightly more sulphuric acid (100 parts, sp. gr. 1.44) than is required to liberate the thiocyanic acid, are mixed, on standing orange-coloured crystals of perthiocyanic acid separate out:



When heated above $220^\circ C.$, perthiocyanic acid decomposes into carbon disulphide, ammonia, sulphur, and a residue of composition which varies according to the temperature. On hydrolysis with water the main reaction is:



Heated with concentrated sulphuric acid, perthiocyanic acid gives sulphur dioxide, carbon dioxide, thiourea, thiocyanic acid and ammonium sulphate. Heated with chlorine the acid gives cyanogen chloride, sulphur chloride, hydrogen chloride and a reddish-brown insoluble residue. Ferric chloride gives a coloration similar to that produced with thiocyanic acid.¹⁰

Perthiocyanogen, $HC_3N_3S_3$, is a yellow, amorphous powder, insoluble in water, alcohol, ether and concentrated sulphuric acid; it

¹ See this Series, Vol. IX, Part II., p. 237.

² See this Series, Vol. VII., Part III., p. 99.

³ See Pacello and Foa, *Gazzetta*, 1923, 53, 526.

⁴ Ephraim, *Helv. Chim. Acta*, 1920, 3, 800.

⁵ Allen and Middleton, *Proc. Indiana Acad. Sci.*, 1922, p. 153.

⁶ Sand, *Ber.*, 1903, 36, 1436.

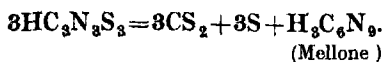
⁷ Fleischer, *Annalen*, 1875, 179, 204.

⁸ Klason, *J. prakt. Chem.*, 1888, [2], 38, 383.

⁹ Hofmann, *Ber.*, 1888, 18, 2201.

¹⁰ Chattaway and Stevens, *Trans. Chem. Soc.*, 1897, 71, 607. For various reduction products of perthiocyanic acid, see Chattaway and Stevens, *ibid.*, p. 833. For the constitution of dithiocyanic and perthiocyanic acids, see Hantzsch and Wolvekamp, *Annalen*, 1904, 331, 265.

can be obtained by the action of chlorine or boiling dilute nitric acid on an aqueous solution of potassium thiocyanate. It is decomposed by heat according to the equation : ¹



With concentrated potassium hydroxide solution thiocyanic acid is obtained.

Compounds of Cyanogen with Hydrogen Sulphide.—The two gases cyanogen and hydrogen sulphide do not react when dry, but when moist they combine in the proportions of 1 molecule of cyanogen with either 1 or 2 molecules of hydrogen sulphide. When the cyanogen is in excess the product is the monosulphide, while the disulphide is produced with excess of hydrogen sulphide. When boiled with alkalis these compounds yield the alkali sulphide and ammonium oxalate. The *monosulphide*, $\text{C}_2\text{N}_2\cdot\text{H}_2\text{S}$, crystallises in yellow needles, odourless but possessing a bitter taste, soluble in water, alcohol or ether. The *disulphide*, $\text{C}_2\text{N}_2\cdot 2\text{H}_2\text{S}$, yields small, brilliant, opaque, orange crystals, soluble in water, alcohol, ether and sulphuric acid.

¹ Glutz, Ber., 1870, 3, 346.

CHAPTER IV.

SELENIUM.

Symbol, Se. Atomic weight, 79.2.

Occurrence.—Although a relatively rare element, selenium is fairly widespread in nature,¹ being frequently found in small quantities both in the combined state in pyrites and sulphide ores² and also in the free state in the volcanic sulphur deposits³ of Italy, Hawaii and the Lipari Islands. In the sulphur deposits the selenium is usually present in the form of an isomorphous mixture with the sulphur. Its occurrence in Swedish pyrites (from Falun) led to the discovery of the element by J. J. Berzelius in 1817,⁴ during an examination of the deposit formed in the lead chambers of a sulphuric acid plant. Owing to the striking chemical resemblance of the new element to tellurium (see p. 351), Berzelius assigned it the name selenium (Gk. *selene*, the moon), which, in order to indicate the metalloid nature of the element, is sometimes modified into selenion.

Selenium also occurs as the main negative constituent in certain minerals; thus selenides of iron, cadmium, lead, copper, silver and mercury are found to a limited extent, particularly in South America. The following are the more important of such minerals: *clausenthalite*, PbSe; *crookesite*, (CuTlAg)₂Se; *eucairite*, CuSe.Ag₂Se; *lehrbachite*, PbSe.HgSe; *onofrite*, HgSe.4HgS; and *zorgite*, a double selenide of lead and copper, which may contain up to 31 per cent. of selenium. Certain selenites, for example of lead and copper, are also found in small quantities.⁵ None of these minerals is of importance as a source of selenium, however.

Selenium in the form of the dichloride may also occur in commercial hydrochloric acid produced by heating sodium chloride with seleniferous sulphuric acid.⁶

As to whether or not selenium is a definite constituent of animal and vegetable organisms is a matter of dispute.⁷ According to Gassmann⁸

¹ For the occurrence of selenium in Yorkshire coke, see Smith, *J. Soc. Chem. Ind.*, 1903, 22, 201; in commercial copper, see Violette, *Compt. rend.*, 1870, 70, 729; in tooth and bone, see Gassmann, *Zeitsch. physiol. Chem.*, 1916, 97, 307; in commercial silver, see Debray, *Ber.*, 1876, 9, 851; in a mineral water, see Taboury, *Bull. Soc. chim.*, 1909, [iv.], 5, 865; in rain and snow, see Gassmann, *Helv. Chim. Acta*, 1918, 1, 52, Karrer, *ibid.*, 499.

² Thomson, *Annals Philosophy*, 1821, 18, 52; Sandorfy and Otto, *Annalen*, 1842, 42, 345; Scheurer-Kestner and Rosenstiehl, *Bull. Soc. chim.*, 1868, [ii.], 9, 43; Guichard, *ibid.*, 1900, [iii.], 23, 147; Pilipenko, *Bull. Acad. Sci. Petrograd*, 1909, p. 1113.

³ Stromeyer, *Ann. Phys. Chem.*, 1824, [ii.], 2, 410; Del Rio, *ibid.*, 1836, [ii.], 39, 526; Brown, *Amer. J. Sci.*, 1916, 42, 132.

⁴ Berzelius, *Ann. Chim. Phys.*, 1818, [ii.], 9, 239, 356; *Ann. Phys. Chem.*, 1826, [ii.], 7, 242; 8, 423; *Annalen*, 1844, 49, 253; *Traité de Chimie*, 1830, II., 397. See also Nordström, *Ber.*, 1879, 12, 1723.

⁵ Moles and Pinà de Rubies, *Anal. Fis. Quim.*, 1913, 11, 73.

⁶ Fritsch, *Zeitsch. physiol. Chem.*, 1918, 104, 59.

⁸ Gassmann, *ibid.*, 1917, 100, 182.

healthy teeth contain about 0.056 per cent. of selenium and the element is present to practically the same extent even in diseased teeth. Most vegetables, and especially spinach, contain traces of selenium, while urine contains 0.0011 per cent. of selenium in the male and 0.00009 per cent. in the female person.

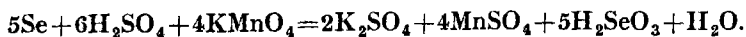
Extraction.—(1) *From Pyrites.*—In the oxidation of the pyrites (or other sulphur mineral) for the formation of sulphur dioxide in the manufacture of sulphuric acid, foreign elements like arsenic and selenium also undergo oxidation and pass off as vapours with the sulphur dioxide. The selenium dioxide produced in this manner then suffers more or less complete reduction by the sulphur dioxide, when finely divided selenium separates, mainly in the lead chambers, as a red, amorphous powder, accompanied possibly by some of the greyish-black form; a portion of the dioxide is also found in the Glover tower acid. The amount of selenium in the chamber "mud" depends, of course, on the nature of the pyrites; relatively large quantities of compounds of arsenic, zinc, tin, lead, iron, copper or mercury are always present, arising almost entirely from impurities in the pyrites.

In the smelting of copper ores some selenium is found in the flue dust; the amount may be as much as 12 per cent., whilst some passes into the anode slimes of the electrolytic refineries.

The method of extraction and purification of the selenium from such mixtures has to be adapted to suit each individual case and the process is therefore frequently lengthy. Generally speaking, most of the methods involve oxidation of the selenium in the mixture to selenious acid, and precipitation of the element from the latter compound by treatment with sulphur dioxide. With powerful oxidising agents, selenic acid is produced, and this compound must be reduced to selenious acid, generally by boiling with hydrochloric acid, before passing sulphur dioxide.¹

The process first employed on a large scale consisted in steeping coke or pumice in the washed sludge and after drying, igniting in a current of air at such a temperature that the selenium burned to the dioxide without any distilling over unburnt. The sublimate of selenium dioxide was dissolved in water and the element precipitated by treatment with sulphur dioxide. The method, however, was too wasteful, not more than 70 per cent. of the selenium being recoverable. Various oxidising agents have therefore been employed, for example, nitric acid, aqua regia,² a mixture of alkali carbonate and nitrate (with fusion),³ potassium or sodium chlorate, potassium permanganate,⁴ and more recently sodium dichromate, manganese dioxide and concentrated sulphuric acid,⁵ and sulphur trioxide in the form of oleum.⁶

When chlorate or permanganate is used the sludge is first treated with water and dilute sulphuric acid, the oxidising agent then being added slowly and in small quantities (to avoid risk of explosion) until the suspended matter is wholly greyish-white:



¹ See, for example, Dennis and Koller, *J. Amer. Chem. Soc.*, 1919, 41, 949.

² Berzelius, *Traité de Chimie*, 1830, II., 398.

³ Wöhler, *Annalen*, 1859, 109, 375; cf. Dennis and Koller, *loc. cit.*

⁴ Koch, *German Patent*, 167457 (1906).

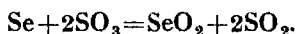
⁵ Garnak, *J. Chem. Ind. Moscow*, 1928, 5, 1424.

⁶ Stahl, *Chem. Zeit.*, 1926, 50, 280; Dyson, *Chemical Age*, 1928, 19, No. 479, *Met. Sec.*, p. 17.

Hydrochloric acid is next added, and, after ten minutes, warm water in considerable quantity. If necessary a little bisulphite may be added to remove any excess of permanganate. After cooling and allowing all suspended matter to settle thoroughly, the clear liquid is syphoned off and the selenium precipitated by blowing sulphur dioxide through for four hours. The selenium is then removed, washed and dried.

The use of sodium chlorate possesses certain advantages; it is cheaper than permanganate and a better yield of selenium is obtained, 90 to 95 per cent. being usual; with permanganate the yield is 80 to 85 per cent., some of the selenium remaining in the solution as selenic acid, which is not directly reduced by the sulphur dioxide.¹

The use of oleum is still more satisfactory, and although the yield of selenium (85 per cent.) is not so high as in the chlorate process, oleum is the cheapest oxidising agent, and no selenic acid is produced. The sludge is warmed with oleum containing 20 per cent. SO_3 , oxidation proceeding according to the equation:



The reaction is reversible under the conditions obtaining, but the oxidation may be completed in the presence of excess of sulphur trioxide, the expelled sulphur dioxide being led away and a little oleum containing 80 per cent. SO_3 added. After cooling, very dilute sulphuric acid (about 1 per cent.) is added, the solution allowed to settle for 24 hours, and finally filtered. The selenium is then precipitated with sulphur dioxide in the usual manner.

The sludge which separates from the oxidation process contains sulphates of lead and calcium, and forms a source of the former metal, which is often an important by-product from the selenium extraction.

A further method of extraction of the selenium from the "mud" is based on the solubility of the element in solutions of potassium cyanide, forming selenocyanide. The solution deposits selenium when acidified, and any sulphur is retained in solution as thiocyanic acid.² Treatment with a solution of an alkali hydroxide, or fusion with sodium carbonate (the latter more especially for the extraction of selenium from the dust of the flues between the pyrites burners and the Glover tower), has also been applied, the mass being extracted with water in the latter case. The resulting aqueous solutions deposit selenium on atmospheric oxidation, whilst any extracted sulphur passes mainly to thiosulphate.³

Chlorine also converts the selenium and sulphur of dried "chamber mud" into the volatile chlorides, from which the selenium can be liberated by decomposition with water followed by reduction with an alkali sulphite.⁴

The presence of much selenium in the Glover tower acid imparts a red colour to the liquid. The element can be separated by dilution followed by treatment with sulphur dioxide.⁵

A method applied to dried anode slimes⁶ consists in heating first with concentrated sulphuric acid to convert metals present to sulphates,

¹ Dyson, *loc. cit.*

² Petterson, *Ber.*, 1873, 6, 1466; Nilson, *ibid.*, 1874, 7, 1719; Shimosé, *Chem. News*, 1884, 49, 26.

³ Berzelius, *Ann. Phys. Chem.*, 1826, [ii.], 8, 423.

⁴ Rose, *ibid.*, 1828, 14, 471.

⁵ Personne, *Bull. Soc. chim.*, 1872, [ii.], 18, 173.

⁶ German Patent, 426669 (1925).

and then with an alkali hydrogen sulphate, when selenium distils over above 700°C .

(2) *From the Metallic Selenides*.—With these substances, the chief of which is *zorgite*, or lead-copper selenide, the usual primary process is again one of oxidation. If a powerful oxidising agent such as aqua regia is used, selenic acid is formed. After removal of excess of the oxidising acid by evaporation, and filtering off the separated lead chloride, the selenic acid is reduced to selenious acid by boiling with hydrochloric acid, and the selenium then precipitated by sulphur dioxide.¹

Purification.—The most usual impurities in the crude selenium are lead and calcium sulphates, tellurium and sulphur. The most satisfactory method of purification is distillation, the temperature being gradually raised to about 900°C . Water and any free sulphuric acid escape first, whilst other impurities are left in the still. The latter should be made of cast iron containing 5 to 6 per cent. of silicon, though fused quartz may be employed.² The receiver is kept at about 360°C . so that the selenium is collected in the molten condition and can be cast into ingots. Some of the element remains in the residue and cannot be distilled even at 1000°C .; this is particularly the case when calcium sulphate is the main impurity, and other methods of extraction have then to be used.

Purification may also be effected by oxidation to selenious acid, *e.g.* by heating with dilute nitric acid. On evaporation the solid selenium dioxide may be obtained, and this can be purified by repeated sublimation in a current of dust-free dry air.³ It may then be redissolved in water, the solution acidified with hydrochloric acid, and the selenium precipitated by passing in sulphur dioxide.⁴ For further purification the element can be sublimed in a current of carbon dioxide, and after heating for some time at 100°C . to convert it into the crystalline condition, it may be heated with carbon disulphide to extract any traces of residual sulphur.

The purified selenium of commerce is usually about 99.5 per cent. pure; it may contain a trace of iron and sulphur but is usually free from tellurium.

The Allotropy of Selenium.

The analogy of selenium with sulphur is observable in the occurrence of allotropy, although no rigid relationship can be traced between the various forms of the two elements.

Gaseous Dissociation.—As with sulphur, determinations of the vapour density of selenium give indications of alteration in the molecular condition, the values up to 900°C . suggesting a mixture mainly of Se_3 and Se_2 molecules; below 550°C . there may be a small proportion of Se_3 molecules present, whilst at temperatures above 900°C . it is possible that a few monatomic molecules are formed, but the vapour is then almost entirely composed of Se_2 molecules.⁵

¹ Billandot, *Encyclopédie chimique*, 1883, 5, 198.

² Dyson, *loc. cit.*

³ Marc, *Zeitsch. anorg. Chem.*, 1906, 48, 393; Threlfall, *Proc. Roy. Soc.*, 1907, [A], 79, 167.

⁴ Hugot, *Ann. Chim. Phys.*, 1900, [vii.], 21, 34; Divers and Shimosé, *Chem. News*, 1885, 51, 190.

⁵ Preuner and Brookmøller, *Zeitsch. physikal. Chem.*, 1912, 81, 129; von Wartenberg, *Zeitsch. anorg. Chem.*, 1907, 56, 320; Biltz, *Zeitsch. physikal. Chem.*, 1896, 19, 385; Szarvay, *Ber.*, 1897, 30, 1244; Deville and Troost, *Ann. Chim. Phys.*, 1860, [iii.], 58, 257; *Compt. rend.*, 1863, 56, 891; Vaubel, *Ann. Chim. Phys.*, 1860, [iii.], 58, 273.

Molecular Complexity in Solution.—This also is variable, depending on temperature and concentration as well as on the nature of the solvent. There is, however, a much greater tendency for the larger molecule to dissociate than is the case with sulphur. When dissolved in molten iodine, with which element selenium does not combine, cryoscopic measurements indicate the presence of diatomic molecules, Se_2 , if the concentration of the solution is over 5 per cent., but in more dilute solutions these molecules undergo partial dissociation into the monatomic condition¹ (see p. 305). In molten mercuric chloride selenium ranges from the octa-atomic condition to the tetra-atomic condition in dilute solution; sulphur under similar conditions appears uniformly octa-atomic. In sulphur chloride selenium is apparently monatomic.² In pyrosulphuric acid, metalloidal selenium dissolves as Se_2 , but the "metallic" form (see the following) dissolves as Se .³

In organic solvents dissolved selenium is generally in the form of more complex molecules. In concentrated solutions using, for example, diphenyl or anthraquinone as solvent, the molecular weight of selenium is represented by Se_8 (yellow phosphorus as solvent gives a similar result), whilst in methylene iodide the molecular condition is stated to be represented by Se_{10} . On dilution of these solutions the selenium undergoes disruption into smaller molecules.⁴

Solid Allotropes.—Both amorphous and crystalline varieties of selenium occur. Amorphous selenium is best known as the "vitreous" and the finely divided brick-red forms, which are frequently described as two distinct allotropes; they are, however, identical. The crystalline allotropes include several monoclinic varieties, red to brown in colour, as well as the so-called "metallic" selenium.

Amorphous Selenium.—(1) *Vitreous Selenium.*—When molten selenium is cooled in not too protracted a manner, no definite solidification or crystallisation ensues, but the mass gradually hardens and the product really represents a strongly undercooled liquid like glass. Vitreous selenium is a brittle reddish-brown substance, exhibiting a conchoidal fracture. When finely powdered and viewed in thin layers it has a deep red colour. This form has an average density of 4.28;⁵ the value varies slightly, possibly owing to the presence of other allotropic modifications of the element.

On heating, a gradual softening commences at about 50° C. and the mass slowly changes into a viscous liquid at 150° C., which becomes distinctly mobile at 250° C. When allowed to cool these changes occur in the reverse order until the solid amorphous variety is again reached. If the cooling is very slow some of the "metallic" modification may be formed. The relation of the vitreous form to the "metallic" form is one of *monotropy*, as at all temperatures up to its melting-point the latter is the more stable form; this would be expected from the fact that the amorphous form merely represents the molten substance

¹ Olivari, *Atti R. Accad. Lincei*, 1908, [v.], 17, ii., 389; 1909, [v.], 18, i., 465; 18, ii., 94, 264; 1912, [v.], 21, i., 718; Pellini, *ibid.*, 1909, [v.], 18, i., 463; Beckmann and Faust, *Zeitsch. anorg. Chem.*, 1913, 84, 103.

² Beckmann and Geib, *ibid.*, 1906, 51, 96.

³ Auerbach, *Zeitsch. physikal. Chem.*, 1926, 121, 337.

⁴ Beckmann, *ibid.*, 1897, 22, 609; Beckmann and Hanslian, *Zeitsch. anorg. Chem.*, 1912, 80, 221; *Sitzungsber. K. Akad. Wiss. Berlin*, 1913, p. 886.

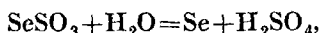
⁵ Cholodny, *J. Russ. Phys. Chem. Soc.*, 1906, 38, 127; Petersen, *Zeitsch. physikal. Chem.*, 1891, 8, 612.

in which crystallisation has not occurred although the normal freezing-point has been passed. At the ordinary temperature the rate of transformation is so slow that vitreous selenium may be preserved indefinitely.¹

(2) *Brick-red Amorphous Selenium*.—When selenium is produced by the reduction of selenious acid with sulphurous acid, glucose or other reducing agent, it is obtained as a brick-red powder. This product is identical with the vitreous form when the latter is in a fine state of division. Its behaviour on heating is the same, and if the pasty mass obtained at 50° C. is cooled, the more massive vitreous modification results. It has been suggested that the name "liquid selenium" should be used to denote these forms of amorphous selenium having no definite melting-point.² Transformation to the vitreous form may also be effected³ by subjecting the red precipitated element to high compression, for example to 10,000 kgms./cm.². On account of the smallness of its particles the brick-red form of amorphous selenium is more reactive than the more massive form, although for full use to be made of this advantage it is obvious that the temperature should not be raised sufficiently either to cause caking or conversion into the "metallic" form.

Both of the foregoing varieties of amorphous selenium are somewhat soluble in carbon disulphide, but selenium chloride, carbon diselenide and methylene iodide are better solvents.⁴ On account of its finer state of division the red form appears more soluble. Discordant results are easily obtained with such solutions because of the tendency to change, especially on warming, into the less soluble crystalline variety—generally the monoclinic form.

The brick-red variety dissolves in concentrated sulphuric acid to give a green solution containing a polymeric form of selenium sulphoxide, SeSO_3 . This slowly decomposes according to the equation



yielding⁵ a *brown allotrope* which is only very sparingly soluble in carbon disulphide. On exposure to sunlight this is slowly converted into an amorphous *black variety*. This black selenium is also produced in small quantity when the reduction of selenious acid with sulphurous acid is effected at 100° C.⁶ The brick-red amorphous form, when exposed to light during seven months, undergoes change and forms *slaty amorphous leaflets*, devoid of lustre.⁷

Crystalline Varieties.—(1) *Monoclinic Selenium* is obtained when a carbon disulphide solution of amorphous selenium is allowed to crystallise, for example by evaporation⁸ or by keeping red amorphous or vitreous selenium in contact with carbon disulphide. In the latter case the

¹ Draper and Moss, *Chem. News*, 1876, 33, 1; Le Chatelier, *Compt. rend.*, 1899, 129, 282.

² Saunders, *J. Physical Chem.*, 1900, 4, 423.

³ von Schrött, *Sitzungsber. K. Akad. Wiss. Wien*, 1906, 115, 1031; *Physikal. Zeitsch.*, 1907, 8, 42.

⁴ Rathke, *Annalen*, 1869, 152, 181; *J. prakt. Chem.*, 1869, 108, 235, 321; Retgers, *Zeitsch. anorg. Chem.*, 1893, 3, 343; Mitscherlich, *Ann. Chim. Phys.*, 1856, [iii.], 46, 301.

⁵ de Coninck, *Compt. rend.*, 1906, 143, 682.

⁶ de Coninck and Chauvenet, *Bull. Acad. roy. Belg.*, 1906, p. 51.

⁷ de Coninck and Reynaud, *ibid.*, 1908, p. 57.

⁸ Mitscherlich, *Ber. Berlin Akad.*, 1855, p. 409; Petersen, *Zeitsch. physikal. Chem.*, 1891, 8, 613; Muthmann, *Zeitsch. Kryst. Min.*, 1890, 17, 354.

relatively unstable amorphous form is the more soluble, so that a gradual separation of the more stable crystalline form ensues.¹

Several varieties of monoclinic selenium are obtainable in this way: reddish-brown leaflets, more deeply coloured granules, or stout prisms of still deeper colouring.²

Monoclinic selenium has a density of 4.44^3 at 0°C . It is only sparingly soluble in carbon disulphide, giving a red solution. When heated rapidly it melts at 170° to 180°C ., but transformation into "metallic" selenium commences to occur slowly near 120°C .⁴ The liquid obtained by rapid heating passes into the vitreous condition when cooled.

(2) *Grey Crystalline Selenium*, "Metallic" Selenium.—This, being the most stable modification of selenium, is obtained by transformation of the preceding forms, but at ordinary temperatures the rate of change is negligibly slow.⁵ Thus amorphous selenium exhibits a very slow transformation at temperatures up to 90°C ., but between this and 217°C . the change is much more rapid and the temperature may rise very considerably on account of the heat liberated. The red crystalline form also gradually undergoes conversion into the "metallic" form at temperatures just over 120°C .⁶ From the foregoing considerations it will be clear that molten selenium below the melting-point of the "metallic" form will slowly tend to change into this form and at 180°C . the molten element soon changes to a semi-crystalline mass.

This form of selenium can also be produced from amorphous selenium by heating with quinoline, pyridine, aniline or other basic organic solvent,⁷ and also by sublimation. In this latter case the sublimate also contains the amorphous form.⁸ Atmospheric oxidation of solutions of alkali selenides gives this variety of selenium as a granular deposit.⁹ When produced by these last three methods, leafy crystals may be obtained, and Muthmann (1890) discovered that crystals which he obtained by the sublimation method were of the trigonal (rhombohedral) system and isomorphous with those of tellurium.

The product from slowly cooled molten selenium is almost black, with a leaden grey surface. It exhibits a fine-grained fracture. It is, however, identical with the foregoing crystals except in its state of aggregation. Both varieties have a density of 4.78 at 0°C . This leaden modification of the element gives a black powder, although when in a very fine state of division a red tint is perceptible. It melts at 217°C . If rapidly cooled from temperatures above its melting-point, vitreous selenium is obtained.¹⁰ The black form has a specific heat of 0.084 and is only sparingly soluble in carbon disulphide. It is soluble

¹ Saunders, *J. Physical Chem.*, 1900, 4, 423.

² Muthmann, *loc. cit.*

³ Cholodny, *J. Russ. Phys. Chem. Soc.*, 1906, 38, 127. Coste (*Compt. rend.*, 1909, 149, 674) gives 4.455 .

⁴ Saunders, *loc. cit.*

⁵ Hittorf, *Ann. Phys. Chem.*, 1851, [ii.], 84, 214; Regnault, *Ann. Chim. Phys.*, 1856, [iii.], 46, 257; Rammelsberg, *Ber.*, 1874, 7, 669; Fabre, *Compt. rend.*, 1886, 103, 53. See also Rathke, *J. prakt. Chem.*, 1869, 108, 235, 321.

⁶ See Coste, *Compt. rend.*, 1909, 149, 674; 1905, 141, 715.

⁷ Saunders, *loc. cit.*

⁸ See Borntraeger, *Dingl. poly. J.*, 1881, 242, 55.

⁹ See Froebel, *Ann. Phys. Chem.*, 1840, [u.], 49, 590; also Fabre, *Ann. Chim. Phys.*, 1887, [vi.], 10, 472.

¹⁰ See Draper and Moss, *Chem. News*, 1876, 33, 1.

in selenium monochloride, yielding the grey crystalline variety on crystallisation.¹

A violet-grey crystalline variety is obtained by melting vitreous selenium at 200° C. and cooling rapidly under pressure. The slender crystals are very sensitive photo-electrically, but are very unstable.²

Colloidal Selenium.

Selenium is readily obtained in the form of a colloidal solution, red by reflected light and blue by transmitted light. Such solutions were first obtained by Schulze³ by the reduction of selenium dioxide in dilute aqueous solution by means of the requisite quantity of sulphur dioxide:



With more concentrated solutions some selenium was also precipitated, which, however, on dilution dissolved in the hydrosol.

When superheated selenium vapour is passed into air-free water, colloidal solutions are formed which are usually rose-coloured, but at first of a blue tint and cloudy. Under the most favourable conditions clear yellowish-red or deep red sols may be obtained,⁴ the former being the more highly dispersed. The blue sols after dialysis are extremely stable, but non-dialysed sols decompose after a few days, selenious acid being detected except in the yellowish-red sols. The dialysed sols may be frozen to an almost colourless ice which at the ordinary temperature thaws and decomposes. The sols are negative and are readily coagulated by the addition of chlorides.

Caoutchouc mixed and warmed with finely divided black amorphous selenium assumes the dark red colour of colloidal selenium. This is the first observed case of the direct reduction of an element to the colloidal condition by intimate contact with a colloid.⁵ The effect is probably due in large measure to stresses produced and heat generated during the mechanical working of the mixture. The presence of another colloidal substance such as albumen, gum arabic or the sodium salt of protalbic acid, renders the colloidal selenium more stable, so that it may even be separated in a solid state without losing its power of again yielding a colloidal solution on the addition of water.⁶

When warmed with neutral organic substances selenium frequently passes into colloidal solution and remains in this condition even after solidification of the solvent. Even when the solid suspension in anthracene or phthalic acid is melted the selenium does not pass into the grey crystalline condition although the points of fusion of these solvents are higher than the transformation temperature. The higher the temperature reached in the preparation of these solutions and the slower the cooling the smaller are the selenium particles.⁷

Selenium prepared by the reduction of selenious acid with sodium or ammonium hydrogen sulphite forms colloidal solutions, that precipitated

¹ Rathke, *Annalen*, 1869, 152, 181.

² Ansel, *Bull. Soc. chim.*, 1916, [iv.], 17, 10.

³ Schulze, *J. prakt. Chem.*, 1885, [2], 32, 390.

⁴ Gutbier and Köhler, *Zeitsch. anorg. Chem.*, 1926, 155, 199.

⁵ Ditmar, *Chem. Zentr.*, 1905, ii., 741.

⁶ Paal and Koch, *Ber.*, 1905, 38, 526.

⁷ Pochettino, *Atti R. Accad. Lincei*, 1911, [v.], 20, i., 428.

by means of the former salt passing more easily into solution than that precipitated by the ammonium salt. Reduction with sodium hydro-sulphite produces reversible and stable sols so long as the relationship $1\text{SeO}_2 : 2$ to $2\cdot8\text{Na}_2\text{S}_2\text{O}_4$ is not exceeded in the reduction.¹

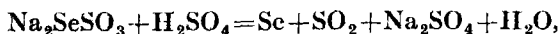
Very stable colloidal solutions of selenium may be prepared by the regulated action of concentrated hydrazine hydrate solution on selenium dioxide or grey crystalline selenium and subsequent dilution of the solutions with water and purification by dialysis. According to the degree of dispersion the colour of the solutions varies from intense yellow to blood red. These sols are completely irreversible. The dilute solutions are stable at the boiling-point, but are readily coagulated by barium sulphate. Sodium and potassium carbonates appear to increase the stability of the system.

Colloidal selenium produced by means of hydrazine hydrate can be frozen to a blue ice which melts with complete coagulation, but the presence in the solution of hydrogen chloride, sodium carbonate or potassium chloride, exerts a protective action which is a maximum at certain definite concentrations.²

If an aqueous solution containing equimolecular quantities of selenium dioxide and dextrose is evaporated on a water-bath to a syrupy consistency and concentrated ammonia is then added, drop by drop, care being taken that the solution remains syrupy, then after cooling and mixing with water, reddish-brown sols of colloidal selenium are obtained. The stability of these sols is increased by the presence of a slight excess of dextrose. They are stable on boiling. If there is no excess of dextrose present then on freezing the sols are completely and irreversibly coagulated. The sols are also sensitive to electrolytes.³

Stable selenium sols may be obtained by the reducing action of quadrivalent titanium. If a solution of titanium trichloride (1.5 per cent.) is boiled for some time, hydrolysis and oxidation occur; on addition of this solution to one of selenium dioxide (0.2 per cent.) reduction to selenium occurs and any unchanged titanous acid, $\text{Ti}(\text{OH})_4$, remains in colloidal solution and exerts a protective action.⁴

By the action of dilute sulphuric acid on sodium selenosulphate according to the equation



particles of colloidal selenium are obtained which are positively charged. The colloidal selenium produced by the solution of selenium in hydrazine hydrate is negatively charged.⁵

The *electrical method*, commonly applied to the preparation of colloidal metals, can also be extended to selenium. When an electric discharge is made to pass under pure water between a platinum anode and a cathode prepared by fusing a small piece of selenium on to platinum foil, colloidal selenium is slowly formed.⁶ When a dilute solution of selenium anhydride is electrolysed using platinum electrodes, a colloidal solution of selenium and a black cathodic deposit of selenium

¹ Guthrie and Heinrich, *Koll. Chem. Beihefte*, 1913, 4, 411.

² See Guthrie and Emslander, *Ber.*, 1921, 54, [B], 1974.

³ Guthrie, *Kolloid-Zeitsch.*, 1923, 33, 334.

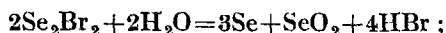
⁴ Guthrie, Ottenstein and Lossen, *Zeitsch. unorg. Chem.*, 1927, 162, 101.

⁵ Meyer, *Zeitsch. Elektrochem.*, 1919, 25, 80-82.

⁶ Müller and Nowakowski, *Ber.*, 1905, 38, 3779.

are formed.¹ According to Gutbier and Weise,² when dilute aqueous selenium dioxide is electrolysed between platinum poles (in the presence of a trace of alkali) with a tension of 220 volts, a moderate evolution of a gas which does not contain hydrogen selenide is first observed. As soon as the solution attains its boiling-point the formation of colloidal selenium commences and the solution becomes consecutively yellow, yellowish-red, red, bluish-red and finally blue. Selenium is not deposited in an irreversible form until the last stage is reached provided that the original solution is not too concentrated. The red solutions invariably show a tendency to become bluish-red when cooled, a sign of incipient coagulation. They can only be obtained in a moderately stable condition if dialysed while still hot and then immediately diluted with pure water or with a solution of a protective colloid such as gum arabic.

Selenium bromide, Se_2Br_2 , decomposes in contact with water according to the equation



a small proportion of the selenium passes into solution, but the greater part is precipitated. Selenium tetrabromide dissolves in water, but much more readily in hydrobromic acid, and on dilution of the acid solution colloidal selenium is formed, which may be purified by dialysis.³

Effect of Freezing on Colloidal Selenium.—The coagulation of selenium sols is greatly accelerated by freezing. It has been shown that the destruction produced by freezing is greater the more completely the solutions have been purified by dialysis. The nature of the reducing agent employed in the preparation of the sols and the temperature of the preparation also have a great influence on the stability towards freezing. The more concentrated sols are more readily destroyed than the more dilute sols, but even with the latter it is found that on keeping the sol in the frozen state for some time a non-homogeneity is produced and a red ring of precipitated selenium formed at the top and bottom of the frozen mass.

With selenium sols prepared by means of hydrazine hydrate at the ordinary temperature, by pouring into a large volume of water it has been shown that the stability of the colloid depends mainly on the degree of dispersion. An optimum concentration of electrolyte is necessary for the stability of the hydrosols. In the absence of electrolytes the system is quite unstable towards freezing.

The sodium salts of protalbic and lysalbic acids exert a protective action on selenium sols.⁴ Saponin also exerts a protective action on sols prepared by the reduction of selenious acid with hydrazine hydrate. The protected sols after dialysis may be preserved for long periods; although they have the tendency to settle into two layers, they may readily be made homogeneous again by simply shaking. Sols prepared in this way are relatively stable towards concentration either by freezing or warming.⁵ A chloroform extract of the seeds of *plantago psyllium* renders selenium sols prepared by reduction with hydrazine hydrate

¹ Pochettino, *Atti R. Accad. Lincei*, 1909, [v.], 18, ii., 544.

² Gutbier and Weise, *Ber.*, 1919, 52, [B], 1374.

³ Gutbier and Engeroff, *Kolloid-Zeitsch.*, 1914, 15, 193, 210.

⁴ Gutbier and Emslander, *ibid.*, 1922, 30, 97; Gutbier and Flury, *ibid.*, 1921, 29, 161.

⁵ Gutbier and Rhein, *ibid.*, 1923, 33, 35.

very stable. Evaporation of such stabilised colloidal solutions gives reversible residues containing up to 65 per cent. of selenium.¹

The rate of flocculation of selenium sols by solutions of potassium or barium chloride of various concentrations at temperatures between 15° and 20° C. has been determined.² Results show that a very high concentration of these electrolytes is necessary for rapid flocculation. Smoluchowski's theory holds when the velocity of flocculation is not far removed from that obtaining when the colloidal particles are totally discharged. The results, however, deviate largely from this theory when the concentrations of the electrolytes are lower.³

General Physical Properties of Selenium.

Selenium boils at about 690° C.,⁴ forming a vapour the colour of which is intermediate between that of chlorine and that of sulphur. The element can be sublimed and distilled at a much lower temperature under very low pressure.⁵ When selenium is heated on charcoal the vapour has an odour resembling that of rotten radishes; this has been attributed to the formation of a small quantity of selenium sub-oxide, but it is more probably due to the formation of carbon diselenide.⁶

The thermal conductivity of selenium depends upon the allotropic form, its age, and the temperature. As might be expected the value for the grey metallic form is greater than that for the vitreous modification; thus at 25° C. the thermal conductivity of the former varies between 0.00070 and 0.00183, whilst that of the latter lies between 0.000293 and 0.000328. The values generally increase with rise in the temperature of preparation of the sample, and with exposure of the sample to light; on the other hand, the conductivity diminishes with age.⁷

The mean specific heats of the various forms are given in the following table :⁸

Allotropic Form.	Temperature Range, ° C	Mean Specific Heat
Vitreous	15-100	0.106
Red crystalline	15- 75	0.082
Metallic	15- 75	0.078
"	15-217	0.084
Liquid	217-300	0.118

The heat of transformation of vitreous selenium to the "metallic"

¹ Gutbier, Huber and Eckert, *Kolloid-Zeitsch*, 1923, 32, 255.

² Krzyt and van Arkel, *ibid.*, 1923, 32, 29.

³ The adsorption of crystal-violet on colloidal selenium has been studied by van der Grinten, *J. Chim. phys.*, 1926, 23, 209.

⁴ Mitscherlich, *Ann. Chim. Phys.*, 1856, [iii.], 46, 301. Carnelley and Williams, *Chem. News*, 1879, 39, 286; Troost, *Compt. rend.*, 1882, 94, 1508; Le Châtelier, *ibid.*, 1895, 121, 325; Berthelot, *ibid.*, 1902, 134, 705.

⁵ Krafft and others, *Ber.*, 1903, 36, 1690, 4344.

⁶ Rathke, *Ber.*, 1903, 36, 600.

⁷ Sayce, *J. Proc. Roy. Soc. N.S. Wales*, 1917, 51, 356; Bellati and Lussana, *Gazzetta*, 1887, 17, 391; *Ber.*, 1888, 21, 132.

⁸ Mondain-Monval, *Compt. rend.*, 1926, 182, 1465; *Bull. Soc. chim.*, 1926, [iv.], 39, 1349.

form at 180° C. is 13.5 calories per gram; with rise in temperature this value increases until at the melting-point, 217° C., it is identical with the latent heat of fusion, namely, 16.4 calories per gram. The heat of transformation of the red crystalline variety to the "metallic" form at 150° C. is 2.2 calories per gram.¹ The heat of dissociation of diatomic selenium has been found by the optical method to be 84,000 gram-calories.² The element is diamagnetic.³

The *electrical conductivity* of selenium is exceedingly small at ordinary temperatures and in the dark, but with rise in temperature or on exposure to light the resistance diminishes in a remarkable and unique manner. The conductivity also depends on the allotropic form and its previous history; the grey metallic form is the most sensitive to these changes, and on heating any other form the rate of transformation into the "metallic" variety considerably influences the actual value of the conductivity. In general the electrical conductivity of selenium increases first rapidly and then more slowly with rise in temperature up to the boiling-point, 690° C. On cooling, it decreases again at the same rate, but if the cooling is protracted, the conductivity of the resulting grey selenium is not constant for a given temperature, but can be diminished at will by slight heating and re-cooling.⁴

On exposure to light, the resistance of selenium immediately sinks to a value which is only a few thousandths of the value in the dark; even exposure for 0.001 sec. will produce a considerable effect.⁵ This phenomenon was first observed by Willoughby Smith⁶ in 1873. When the light is shut off the resistance increases, somewhat slowly, becoming normal in a short time, however. Very feeble rays, such as the light from a star, can produce an appreciable effect on the resistance. All visible rays are effective, but the influence is most intense in the case of the red, of wave-length about 700 $\mu\mu$.⁷ Ultra-violet rays, Röntgen rays, cathode rays and rays from radioactive substances act in the same way.⁸ In the case of the last-named, the effect of the γ -rays is small compared with that of the β -rays. Temperature has little effect on the influence of light, the sensitivity of the selenium only being reduced by 10 to 25 per cent. at the temperature of liquid air.⁹ It is upon this action towards light that the extremely sensitive photo-electric selenium cell depends.¹⁰ Such cells are employed in the construction

¹ Mondain-Monval, *loc. cit.*

² Rosen, *Zeitsch. Physik*, 1927, 43, 69.

³ Carnelley, *Chem. News*, 1879, 40, 183. See also Heaps, *J. Opt. Soc. Amer.*, 1927, 15, 190.

⁴ Pélabon, *Compt. rend.*, 1921, 173, 295, 1466. See also Datta, *Phil. Mag.*, 1920, [6], 42, 463.

⁵ Thirring, *Zeitsch. techn. Physik*, 1922, 3, 118.

⁶ See Smith, *Nature*, 1873, 7, 303; May and Smith, *Ber.*, 1873, 6, 204; *Dingl. poly. J.*, 1873, 207, 512; *Amer. J. Sci.*, 1873, [iv.], 5, 301.

⁷ Amaduzzi, *Il selenio* (Bologna, 1904); Gudden and Pohl, *Zeitsch. Physik*, 1925, 35, 243.

⁸ Guilleminot, *Compt. rend.*, 1913, 157, 1155; Nicholson, *Physikal. Zeitsch.*, 1913, 14, 1210, 1212; Perrot, *Compt. rend.*, 1899, 129, 956; Block, *ibid.*, 1901, 132, 914. See also van Aubel, *ibid.*, 1903, 136, 929, 1189; Griffiths, *ibid.*, 1903, 137, 647; Del Regno, *Atti R. Accad. Lincei*, 1926, [vi.], 3, 201; Phillips, *Nature*, 1929, 123, 681.

⁹ Carpini, *Atti R. Accad. Lincei*, 1905, [v.], 14, n. 667.

¹⁰ For the construction of selenium cells, see Siemens, *Ann. Phys. Chem.*, 1875, [n.], 156, 334; Bidwell, *Phil. Mag.*, 1885, [v.], 20, 178; 1895, [v.], 40, 1233; Brown, *Physikal. Zeitsch.*, 1910, 11, 481; Angel, *Bull. Soc. chim.*, 1915, [iv.], 17, 10; Mundy, *Sci. News*, 1924, 1, 25. See also Fournier d'Albe, *The Moon-element* (Fisher Unwin, Ltd., 1925), pp. 38-45.

of the photophone, by means of which speech may be transmitted by a beam of light. The first transmitter of this kind was made in 1880 by Graham Bell, the inventor of ordinary telephony.¹ Another instrument, the optophone, invented by Fournier d'Albe,² makes it possible for the blind to read ordinary books and newspapers by sound.

In order to explain this remarkable property of selenium many theories have been put forward,³ most of which are now untenable, and only two need be considered.

It was first suggested by Siemens⁴ in 1875, and the hypothesis was strongly supported by later investigations,⁵ that crystalline selenium exists in two forms "A" and "B," "A" being a non-conductor and "B" a good conductor of electricity. In the dark the equilibrium mixture consists almost entirely of "A"; the equilibrium is displaced in the direction of "B" both by the action of heat and by exposure to light:



The isolation of the two modifications was described by Pélabon, but was not confirmed by later investigation. The theory is discounted by the fact that at exceedingly low temperatures the action of light is only slightly diminished, whereas it would be expected that such a transformation would no longer proceed.

However, Briegleb,⁶ from X-ray investigations, maintains that in all the allotropic modifications two such pseudo-components do exist, and that these may be separated in some degree by taking advantage of the fact that although their absolute solubilities in carbon disulphide are almost identical, the rates at which they dissolve are different. By spectroscopic methods evidence has been obtained that the two forms exist in equilibrium in this solution and that the equilibrium varies with the temperature.

What appears to be a more satisfactory explanation and one largely favoured by physicists is that the phenomenon is an effect of purely electronic character. The actual mechanism of the action is not yet completely understood, but the light appears to cause ionisation at the surface of the selenium, with immediate increase in conductivity.⁷ The splitting off of electrons may be not only from the selenium atoms but also from the incident stream. It has also been suggested that the

¹ See Rankine, *Nature*, 1920, 104, 604.

² Fournier d'Albe, *loc. cit.*

³ Spath, *Zeitsch. Physik.*, 1922, 8, [3], 165; Fournier d'Albe, *loc. cit.*, chap. iii.

⁴ Siemens, *Ann. Phys. Chem.*, 1875, [ii.], 156, 334; 1876, 159, 117; 1877, [iii.], 2, 521; *Phil. Mag.*, 1875, [iv.], 50, 416.

⁵ Berndt, *Physikal. Zeitsch.*, 1904, 5, 121, 289; Marc, *Ber.*, 1906, 39, 697; *Zeitsch. anorg. Chem.*, 1907, 53, 298; 1914, 85, 65; Kruyt, *ibid.*, 1909, 64, 305; Berger, *ibid.*, 1914, 85, 75; Pélabon, *Compt. rend.*, 1921, 173, 1466; 1922, 174, 391. See also Sale, *Proc. Roy. Soc.*, 1873, 21, 283; Adams, *ibid.*, 1875, 23, 535; 1876, 24, 163; 1877, 25, 513; Rosse, *Phil. Mag.*, 1874, [iv.], 47, 161; Pfund, *ibid.*, 1904, [vi.], 7, 26; Hesehus, *Physikal. Zeitsch.*, 1906, 7, 163; J. Russ. Phys. Chem. Soc., 1884, 15, 125, 146; Pochettino, *Nuovo Cim.*, 1912, [vi.], 4, 189.

⁶ Briegleb, *Naturwiss.*, 1929, 17, 51.

⁷ See Hesehus, *Physikal. Zeitsch.*, 1906, 7, 163; von Schrott, *ibid.*, 1907, 8, 42; Pfund, *ibid.*, 1909, 10, 340; Ries, *ibid.*, 1911, 12, 480, 522; Amaduzzi, *ibid.*, 1912, 13, 165; Fournier d'Albe, *Proc. Roy. Soc.*, 1913, [A], 89, 75; Nicholson, *Physikal. Zeitsch.*, 1913, 14, 1210; Gudden and Pohl, *ibid.*, 1921, 22, 529; 1925, 35, 243; Spath, *Zeitsch. Physik.*, 1922, 8, 165; *Naturwiss.*, 1922, 10, 14; Del Regno, *Atti R. Accad. Lincei*, 1924, [v.], 33, ii. 163; Holmes, *Phys. Review*, 1925, [ii.], 25, 250; Kasarnovskii, *Trans. Karpov Inst. Chem.*, 1925, No. 4, 93; Piersol, *Phys. Review*, 1927, [ii.], 30, 664.

interatomic space occupied by the conducting electrons may be increased. The theory explains why the recovery of the selenium is not immediate when the light is removed, and why after exposure to the more deeply penetrating rays, such as the X-rays, the recovery is even slower.

Spectrum.—The emission,¹ absorption² and fluorescence³ spectra have been investigated. According to de Gramont,⁴ selenium gives neither *raies ultimes* nor *raies de grande sensibilité*. The most persistent lines of the emission spectrum are (in Å), 1960·2, 2039·7, 2062·6, 4730·9, 4739·1 and 4742·3,⁵ and Kimura⁶ has observed that non-luminous selenium vapour absorbs the lines 1960 and 2040 Å. The vapour, when excited by intense illumination from a quartz-mercury arc, exhibits⁷ at 325° C. a fluorescence spectrum extending from 5079 to 2229 Å, apparently analogous to the ultra-violet fluorescence spectrum of iodine; with rise in temperature this spectrum disappears and at 430° C. is replaced by one containing nine faint broad bands extending from 4178 to 4829 Å.⁸

Chemical Properties of Selenium.

In its general chemical behaviour, selenium occupies an intermediate position with respect to sulphur and tellurium. It combines directly with many elements, e.g. oxygen, hydrogen, fluorine, chlorine, bromine and most metals.⁹ Details of some of its compounds will be given later,

¹ Plucker and Hittorf, *Phil. Mag.*, 1864, [iv.], 28, 64; Salet, *Compt. rend.*, 1871, 73, 742; Eder and Valenta, *Denkschriften der kaiserlichen Akad. Wiss. Wien*, 1893, 60, 307; de Gramont, *Compt. rend.*, 1895, 120, 778; Berndt, *Ann. Physik*, 1903, [iv.], 12, 1115; Messerschmidt, *Zeitsch. wiss. Photochem.*, 1907, 5, 249; McLennan and Young, *Phil. Mag.*, 1918, [vi.], 36, 450; McLennan, McLay and McLeod, *ibid.*, 1927, [vii.], 4, 486; Sawyer and Humphreys, *Phys. Review*, 1928, [ii.], 32, 583. For high frequency emission spectra, see Siegbahn and Friman, *Ann. Physik*, 1916, [iv.], 49, 611; Bloch and Bloch, *Compt. rend.*, 1927, 185, 761.

² van Assche, *Compt. rend.*, 1883, 97, 838; Gernez, *ibid.*, 1872, 74, 1190; Lockyer and Roberts, *Proc. Roy. Soc.*, 1875, 23, 344; Wood, *Phil. Mag.*, 1902, 3, 607; Meier, *Ann. Physik*, 1910, 31, 1017; Koemgsberger and Kupferer, *ibid.*, 1912, 37, 601; Rosen, *Zeitsch. Physik*, 1927, 43, 69.

³ Steubing, *Physikal. Zeitsch.*, 1913, 14, 887; Diestelmeier, *ibid.*, 1913, 14, 1000; *Zeitsch. wiss. Photochem.*, 1915, 15, 18; Rosen, *loc. cit.*

⁴ de Gramont, *Compt. rend.*, 1920, 171, 1106.

⁵ International Critical Tables, 1929.

⁶ Kimura, *Japan J. Phys.*, 1927, 4, 81.

⁷ McLennan, Walerstein and Grayson Smith, *Phil. Mag.*, 1927, [vii.], 3, 390.

⁸ For the refractive indices of selenium, see Cuthbertson and Metcalfe, *Phil. Trans.*, 1907, A, 207, 135; Dodd, *J. Amer. Chem. Soc.*, 1920, 42, 1579. Also Becquerel, *Ann. Chim. Phys.*, 1877, [v.], 12, 5; Wood and Pfund, *Phil. Mag.*, 1902, [v.], 3, 607; Zoppellari, *Gazzetta*, 1894, 24, ii., 340; Sirks, *Ann. Phys. Chem.*, 1871, [ii.], 143, 429; Kyropoulos, *Zeitsch. Physik*, 1926, 40, 618; Nicol, *J. Proc. Roy. Soc. N.S.W.*, 1926, 60, 60. For the ionisation potential of selenium vapour, see Udden, *Phys. Review*, 1921, 18, 385; Piccardi, *Atti R. Accad. Lincei*, 1927, (vi.), 6, 305, 428. For light-positive and light-negative photo-phoresis in connection with sulphur and selenium, see Parankiewicz, *Ann. Physik*, 1918, [iv.], 57, 489.

⁹ Berzelius, *Schweigger's J.*, 1822, 34, 79; Orłowsky, *Ber.*, 1881, 14, 2823; Obach, *J. prakt. Chem.*, 1878, [ii.], 18, 278; Fonze-Diacon, *Compt. rend.*, 1900, 130, 1314 (Al—Se); Margottet, *ibid.*, 1877, 84, 1293; 85, 1142; Bidwell, *Phil. Mag.*, 1895, [v.], 40, 233; Heyn and Bauer, *Metallurgie*, 1906, 3, 73 (Cu—Se); Chrétien, *Compt. rend.*, 1906, 142, 1339, 1412 (Sb—Se); Friedrich and Leroux, *Metallurgie*, 1908, 5, 355 (Cu—Se, Ag—Se, Pb—Se); Pellini, *Atti R. Accad. Lincei*, 1909, [v.], 18, ii., 211 (Hg—Se); Biltz and Mecklenburg, *Zeitsch. anorg. Chem.*, 1909, 64, 226 (Sn—Se); Pélabon, *Compt. rend.*, 1906, 142, 207 (Sb—Se); 1907, 145, 118 (Ti—Se); 1907, 144, 1169 (Pb—Se); *Ann. Chim. Phys.*, 1909, [viii.], 17, 526; *Compt. rend.*, 1911, 152, 1302; 153, 342; 1914, 158, 1669 (Sb—Se); 158, 1895 (Sn—Se); Parravano, *Gazzetta*, 1913, 43, i., 201 (Bi—Se);

whilst descriptions of others will be found under the heading of the companion element in other volumes of this series. In the molten condition selenium is partially or completely miscible with many metals, e.g. antimony, lead, copper, bismuth, silver and gold, the fused mass constituting a mixture of the metallic selenide and the element present in excess. Antimony thus yields selenides of compositions Sb_2Se_3 and SbSe ,¹ bismuth similarly gives the selenides Bi_2Se_3 and BiSe ,² copper forms cuprous selenide, Cu_2Se , and silver the selenide Ag_2Se . By completely fusing selenium with sodium in an atmosphere of hydrogen the existence of a series of selenides Na_2Se , Na_2Se_2 , Na_2Se_3 , Na_2Se_4 and Na_2Se_6 , analogous to the sulphides and polysulphides, has been shown.³ Selenium combines with sodium or potassium dissolved in liquid ammonia, producing the monoselenide Na_2Se or K_2Se , or the tetraselenide Na_4Se_4 or K_4Se_4 , according to the relative proportions of the two elements present.⁴

Selenium reduces hot aqueous solutions of silver or gold salts with the formation of silver selenide or metallic gold, respectively.⁵ In the case of silver salts the reaction corresponds with the equation: ⁶



The element is unaffected by water, but in a fine state of division hydrogen peroxide oxidises it to selenic acid. Ozone in the presence of water gives a similar result.⁷

Selenium is soluble in sulphuric acid, forming a green solution which, in the case of the "metallic" form, probably contains a compound of composition SO_3Se (p. 338), and in the case of the red amorphous variety, a polymeric form of this compound.⁸ The presence of selenium does not affect the electrical conductivity of sulphuric acid. Dilute aqueous potassium hydroxide dissolves the red variety, producing a solution which probably contains polyselenides; in the presence of sodium hydrosulphite, however, only sodium selenide, Na_2Se , is obtained.⁹

When selenium is heated with a metallic oxide or carbonate, a mixture of selenide and selenite is commonly obtained. At high temperatures selenium is able to displace sulphur partially from sulphides such as copper sulphide and silver sulphide, the effect probably being due to selenium being less volatile than sulphur.¹⁰ At ordinary temperatures

43, i., 210 (Sb—Se); Pellini, *Gazzetta*, 1915, 45, i., 533 (Ag—Se); Murakami, *Mem. Coll. Sci. Kyōto*, 1915, 1, 153 (Ti—Se); Kimata, *ibid.*, 1915, 1, 119 (Te—Se); Tomoshige, *ibid.*, 1920, 4, 55 (Bi—Se).

¹ Kremann and Wittek, *Zeitsch. Metallkunde*, 1921, 13, 90. See also Pélabon, *Ann. Chim.*, 1920, [ix.], 13, 121.

² Tomoshige, *Mem. Coll. Sci. Kyōto*, 1920, 4, 55.

³ Mathewson, *J. Amer. Chem. Soc.*, 1907, 29, 867. See also Rosenfeld, *Ber.*, 1891, 24, 1660.

⁴ Hugot, *Compt. rend.*, 1899, 129, 299.

⁵ Hall and Lenher, *J. Amer. Chem. Soc.*, 1902, 24, 918. Also Friedrich, *Zeitsch. angew. Chem.*, 1902, 15, 852; Guyot, *Compt. rend.*, 1871, 72, 685; Senderens, *ibid.*, 1887, 104, 175.

⁶ Garelli and Angeletti, *Atti R. Accad. Lincei*, 1922, [v.], 31, ii. 440.

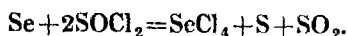
⁷ Maitfert, *Compt. rend.*, 1882, 94, 1186.

⁸ Moles, *Anal. Fis. Quim.*, 1915, 13, 134.

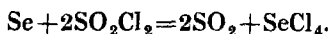
⁹ Tschugaev and Chlopin, *Ber.*, 1914, 47, 1269; *J. Russ. Phys. Chem. Soc.*, 1915, 47, 364. For the anodic formation of polyselenides by the action of alkali on selenium, see Le Blanc, *Zeitsch. Elektrochem.*, 1905, 11, 813; 1906, 12, 649; Müller and Nowakowski, *ibid.*, 1905, 11, 931.

¹⁰ Potilitzen, *Ber.*, 1870, 12, 697.

selenium has practically no action on thionyl chloride, but when heated in thionyl chloride vapour selenium tetrachloride is formed according to the equation:



Sulphuryl chloride, on the other hand, is attacked by selenium at ordinary temperatures, selenium tetrachloride again being formed: ¹



Pyrosulphuryl chloride, $\text{S}_2\text{O}_5\text{Cl}_2$, converts selenium into a colourless crystalline compound, SeSO_3Cl_4 or $\text{SeCl}_4 \cdot \text{SO}_3$, generally known as sulphur-selenium oxytetrachloride ² (p. 321), which melts at 165°C . and boils at 185°C ., and which can also be obtained by the combination of its constituents, selenium tetrachloride and sulphur trioxide. ³

Applications of Selenium.

The remarkable variation in the electrical conductivity of "metallic" selenium on exposure to light, renders the element of great importance for the construction of certain types of optical apparatus. ⁴ For this purpose the element is generally used in the form of thin sheets which have been carefully "annealed" by heating for some time at 200°C . in order to ensure transformation to the "metallic" form. The difficulty in connection with "fatigue" or the slow recovery of normal resistance after exposure to light is usually surmounted by employing a series of cells on a rotating disc or other device whereby each cell is given time to recover while others are in use. The photophone and the optophone have already been mentioned. The gradual development of photo-telegraphy, the talking film and television, owes much to the application of selenium, although alternative methods are now available. Faint sources of light, such as the light of stars, may be measured by the use of selenium; the lights of lighthouses and of buoys may be regulated from a distance or by the disappearance of daylight, and the density of smoke or vapours in reaction chambers may be automatically recorded by apparatus employing the element. Explosive charges may be fired from a distance by means of a beam of light and a selenium cell, whilst the interruption of such a beam focussed on to a selenium cell constitutes a serviceable burglar alarm. The amount of selenium at present used for such purposes, however, is very small. ⁵

The chief use of selenium and its compounds is in the glass and ceramic industries. ⁶ The grey crystalline form is generally used. In the former industry the element is employed on an increasing scale for four purposes: (a) for decolorising glass—half an ounce of selenium

¹ Lenher and North, *J. Amer. Chem. Soc.*, 1907, 29, 33.

² Prandtl and Borinski, *Zeitsch. anorg. Chem.*, 1909, 62, 237.

³ Rose, *Ann. Phys. Chem.*, 1838, [ii.], 44, 315.

⁴ See Ruhmer, *Das Selen und seine Bedeutung für die Elektrotechnik* (Berlin, 1902).

⁵ See further, Ries, *Das Selen* (Munich, 1918); Fournier d'Albe, *The Moon-element* (Fisher Unwin, Ltd., London, 1925); Thirring, *Zeitsch. techn. Physik*, 1922, 3, 118; Logan, *J. Ind. Eng. Chem.*, 1923, 15, 40; Lauste, *Scientific American*, 1917, Dec. 22. For the use of selenium cells as colorimeters, see Mickwitz, *Zeitsch. anorg. Chem.*, 1928, 171, 285; 176, 27.

⁶ Krak, *Glass Ind.*, 1928, 9, No. 7, 152; Dyson, *Chemical Age*, 1928, 19, No. 479, *Met. Sec.*, p. 17; Silverman, *J. Amer. Ceram. Soc.*, 1928, 11, 81; Polgrean, *Trans. Ceram. Soc.*, 1929, 28, 87. See also *Chem. News*, 1912, 106, 309.

with a little cobalt oxide is added to 1000 lb. of sand; (b) for producing pink- and orange-coloured glassware—the selenium is added to soda-lime or potash-soda glasses under oxidising conditions (the orange colour is produced by a mixture of selenium and uranium); (c) for producing ruby glass—more selenium than in the previous operations is added,¹ together with cadmium sulphide, a distinctive ruby colour of considerable intensity resulting; (d) for producing amber glass, a brilliant glass suitable for high grade table ware—selenium and borax are added to lead glass under oxidising conditions. Instead of the element, sodium or barium selenite is now used by many glass makers in order to avoid loss by volatilisation. Selenium is also used to produce ruby glazes in pottery.

Electric cables treated with a thin layer of metallic selenium are flame-proof to a remarkable degree, thus minimising the risk of fire through short-circuiting of heavy currents. The cotton or rubber used for covering the wire may itself be treated with the selenium and so rendered non-inflammable; flame-proof switchboards, etc., may also be constructed.

Attempts to use selenium either in place of or in conjunction with sulphur in the vulcanisation of rubber do not appear to be completely successful,² although it is claimed that rubber vulcanised with sulphur and selenium in the presence of an organic accelerator exhibits enhanced rigidity and resistance to abrasion.³ The incorporation of powdered selenium in ordinary rubber for vulcanisation by sulphur is said to provide crystalline selenium nuclei which induce the *internal* crystallisation of any superfluous sulphur and so prevent the undesirable surface crystallisation (or "bloom"). The effect is attributed to the isomorphous character of selenium and sulphur.

Certain selenium compounds exhibit bactericidal and fungicidal action,⁴ and selenious acid may be used as a herbicide against dandelion, Canada thistle and burdock.

Certain selenites, for example of barium and lead, are satisfactory as pigments, yielding paints of a high degree of opacity.⁵

Many toning processes in photography involve the use of selenium compounds.⁶ One such process recently recommended consists in treating the print or lantern slide, after developing, fixing and washing, with a solution containing about 1 per cent. of crystalline sodium sulphide and 1 per cent. of sodium selenite or selenious acid; after twenty minutes or so in such a bath intense brown tones are obtained with chlorobromide papers, or brown-violet tones with pure bromide papers.⁷

Physiological Action.

Selenium itself exerts no poisonous action although the alkali selenites and selenates are very poisonous.⁸ The selenates probably owe

¹ A minimum of about 0.25 per cent. Se is required to produce a deep ruby colour.

² See Norris, *India Rubber World*, 1928, 78, No. 4, 60.

³ Boggs and Follansbee, *Trans. Inst. Rubber Ind.*, 1926, 2, 272.

⁴ See Stover and Hopkins, *Ind. Eng. Chem.*, 1927, 19, 510.

⁵ Gardner, *Educational Bur. of Paint Manufacturers' Association, U.S.A.*, Circular 62, 1919.

⁶ For a summary of literature dealing with these processes, see Sedlacek, *Brit. J. Phot.*, 1928, 75, 784; 1929, 76, 4, 29, 44.

⁷ See Milbauer, *Chem. Listy*, 1927, 21, 509.

⁸ Czapek and Weil, *Arch. exp. Path. Pharm.*, 1893, 32, 438; Labes, *ibid.*, 1928, 133, 57; also this volume, p. 359.

their effect to a primary reduction to selenite. The symptoms somewhat resemble those of arsenical poisoning. Some moulds have the power of reducing selenium compounds with the production of an unpleasant faecal odour.¹ Extremely small quantities of sodium selenite increase the crop of moulds belonging to the *Penicillium* genus.²

Atomic Weight.

The first determination of the atomic weight of selenium was due to Berzelius,³ who in 1818 synthesised the tetrachloride, with the following result :⁴

$$\text{Se} : 4\text{Cl} :: 100 : 179, \quad \therefore \text{Se} = 79.23.$$

In 1847 Sacc determined the atomic weight by several methods, of which only two proved of value, namely : (i) pure selenium dioxide was reduced with ammonium hydrogen sulphite and the resulting selenium weighed ; (ii) barium selenite was calcined with sulphuric acid and the resulting barium sulphate weighed. The results were as follows :⁵

$$3 \text{ experiments—SeO}_2 : \text{Se} :: 100.000 : 71.088, \quad \therefore \text{Se} = 78.68.$$

$$4 \text{ experiments—BaSeO}_3 : \text{BaSO}_4 :: 100.000 : 88.437, \quad \therefore \text{Se} = 78.58.$$

A totally different procedure was followed in 1852 by Erdmann and Marchand,⁶ who analysed mercury selenide with the following result :

$$3 \text{ experiments—HgSe} : \text{Hg} :: 100.000 : 71.7327, \quad \therefore \text{Se} = 79.05.$$

In 1860 Dumas⁷ reverted to the original method of Berzelius, but in a series of not very concordant experiments obtained a decidedly higher value for the atomic weight :

$$7 \text{ experiments—Se} : 4\text{Cl} :: 100.000 : 178.652, \quad \therefore \text{Se} = 79.39.$$

Sixteen years later, Ekman and Pettersson⁸ estimated the silver in pure silver selenite by ignition and the selenium in the pure dioxide by reduction with sulphurous acid from its solution in dilute hydrochloric acid. The results were :

$$7 \text{ experiments—Ag}_2\text{SeO}_3 : 2\text{Ag} :: 100.000 : 62.957, \quad \therefore \text{Se} = 78.95.$$

$$5 \text{ experiments—SeO}_2 : \text{Se} :: 100.000 : 71.191, \quad \therefore \text{Se} = 79.08.$$

In 1898 Lenher⁹ made a careful study of the atomic weight of selenium by new methods. Firstly, pure silver selenite was transformed into silver chloride by heating in a stream of hydrogen chloride ; the silver chloride was weighed and then reduced in hydrogen, the resulting silver also being weighed :

¹ Rosenheim, *Proc. Chem. Soc.*, 1902, 18, 138.

² See Němec and Kás, *Biochem. Zeitsch.*, 1921, 114, 21.

³ Berzelius, *Pogg. Annalen*, 1826, 8, 1.

⁴ All atomic weights have been recalculated, using the following antecedent data : O=16.000, H=1.0076, Cl=35.457, Br=79.916, Ag=107.88, N=14.008, S=32.065, Hg=200.6, Ba=137.37, C=12.003.

⁵ Sacc, *Ann. Chim. Phys.*, 1847, [iii.], 21, 119.

⁶ Erdmann and Marchand, *J. prakt. Chem.*, 1852, 55, 202.

⁷ Dumas, *Annalen*, 1860, 113, 32.

⁸ Ekman and Pettersson, *Ber.*, 1876, 9, 1210.

⁹ Lenher, *J. Amer. Chem. Soc.*, 1898, 20, 355.

11 experiments— $\text{Ag}_2\text{SeO}_3 : 2\text{AgCl} :: 100.000 : 83.558, \therefore \text{Se}=79.82.$

8 experiments— $\text{Ag}_2\text{SeO}_3 : 2\text{Ag} :: 100.000 : 62.895, \therefore \text{Se}=79.29.$

Secondly, ammonium bromoselenate was reduced with hydroxylamine hydrochloride and the resulting selenium weighed :

8 experiments— $(\text{NH}_4)_2\text{SeBr}_6 : \text{Se} :: 100.000 : 13.3224, \therefore \text{Se}=79.24.$

In 1901 Steiner¹ published the results of two analyses of selenium diphenyl which were effected by combustion, the resulting carbon dioxide being absorbed and weighed :

2 experiments— $(\text{C}_6\text{H}_5)_2\text{Se} : 12\text{CO}_2 :: 100.000 : 226.536, \therefore \text{Se}=78.98.$

The following year Julius Meyer reverted to the analysis of silver selenite. The analysis, however, was made by electrolytic deposition of the silver from a solution of the salt in potassium cyanide :²

5 experiments— $\text{Ag}_2\text{SeO}_3 : 2\text{Ag} :: 100.000 : 62.9193, \therefore \text{Se}=79.16.$

In 1910 Kuzma and Krehlik³ made a careful re-determination of the atomic weight of the element, the method used being reduction of the dioxide with sulphurous acid. The result was as follows :

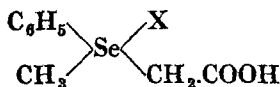
10 experiments— $\text{SeO}_2 : \text{Se} :: 100.000 : 71.2385, \therefore \text{Se}=79.26.$

The value adopted by the Chemical Society on the recommendation of the Sub-Committee on Atomic Weights (1929) is $\text{Se}=79.2.$

According to Aston⁴ selenium is not a simple element, but consists of a mixture of no fewer than six *isotopes*, the atomic masses of which are, in order of intensity, 80, 78, 76, 82, 77, 74. The atomic number of selenium is 34.

Valency of Selenium.

Selenium resembles sulphur in its variations in valency, compounds being known in which the element is definitely bivalent, quadrivalent and sexavalent, respectively. The tendency to quadrivalency, however, is greater than in the case of sulphur, and the compounds formed in which this valency is exhibited are relatively more stable in the case of selenium than in the case of sulphur.⁵ Thus, whilst the bivalent selenium in organic selenides readily combines with a molecular proportion of chlorine or other halogen,⁶ sexavalent selenium in the selenates is easily reduced to the quadrivalent selenious condition. As with sulphur, it has been possible to demonstrate that in quadrivalent selenium the four valencies are disposed in three dimensions of space, since substances of the type



¹ Steiner, *Ber.*, 1901, 34, 570.

² J. Meyer, *Zeitsch. anorg. Chem.*, 1902, 31, 391.

³ Kuzma and Krehlik, *Trans. Bohemian Acad. Emp. Francis Joseph*, 1910, 19, No. 13 ; *Chemiché Listy*, 1910, 5, 6.

⁴ Aston, *Nature*, 1922, 110, 664 ; *Phil. Mag.*, 1923, [vi.], 45, 934.

⁵ von Bartsch, *Chem. Zeit.*, 1907, 31, 347.

⁶ Lyons and Bush, *J. Amer. Chem. Soc.*, 1908, 30, 831.

where X represents an acid radical, are capable of existence in two enantiomorphous forms, the main difference between which lies in the effect of the solutions on polarised light.¹

Constitution of the Selenium Molecule.

Cryoscopic measurements on solutions of selenium in various solvents give divergent results for the constitution of the selenium molecule, the atomicity varying not only with the nature of the solvent but with the temperature and concentration of the solution. In organic solvents, *e.g.* anthraquinone and diphenyl, the molecular weight corresponds with Se_8 , as is also the case in yellow phosphorus.² In methylene iodide (at 4° C.) the results point to Se_8 and Se_{10} . In iodine the values obtained both cryoscopically (at 113.9° C.) and ebullioscopically (at 184° C.) correspond with the diatomic molecule Se_2 , although iodine, on account of its low dielectric constant, would not be expected to show dissociating properties.³ According to Olivari, the molecular weight corresponding with Se_2 is only obtained in solutions having a greater concentration than 5 per cent. of selenium; in more dilute solutions a lower molecular weight is obtained.

The maximum absorption of light⁴ by selenium vapour occurs between 650° and 700° C., and vapour density determinations show that the average molecular weight at this temperature corresponds to Se_8 .

Detection and Estimation of Selenium.

Selenium is recognisable by the characteristic odour, resembling that of rotten radishes, which it emits when warmed, and by its combustion with a blue flame, forming the dioxide. The element and most of its compounds impart a bright blue coloration to the Bunsen flame, and a piece of cold porcelain held in the flame may receive a red deposit of the element in the reducing zone or a white deposit of the dioxide in the oxidising zone. By heating with sodium carbonate in the reducing flame, selenium compounds can be made to yield sodium selenide, from which the characteristic odour of hydrogen selenide will be developed on the addition of acid.⁵

A wet test to identify traces of selenium has been described by Denigès.⁶ The reagent used is a solution of mercurous nitrate prepared by dissolving 10 grams of the salt in a mixture of 10 c.c. of concentrated nitric acid and 100 c.c. of water. Selenious acid and its salts yield a crystalline precipitate of mercurous selenite either immediately or on cooling. This precipitate consists of characteristic long needle-shaped crystals. Solutions containing 0.1 per cent. of the acid will give this reaction. Selenic acid and its salts when treated with an equal bulk of the reagent give a precipitate of mercurous selenate which

¹ Pope and Neville, *Trans. Chem. Soc.*, 1902, 81, 1552.

² Beckmann and others, *Zeitsch. physikal. Chem.*, 1897, 22, 609; 1903, 46, 853; *Zeitsch. anorg. Chem.*, 1912, 80, 221.

³ Olivari, *Atti R. Accad. Lincei*, 1908, [v.], 17, ii, 389; 1909, 18, ii, 264; Beckmann and others, *loc. cit.*, also *Zeitsch. anorg. Chem.*, 1918, 102, 215.

⁴ Dobbie and Fox, *Proc. Roy. Soc.*, June 1920.

⁵ Bunsen, *Annalen*, 1866, 128, 257. See also Fresenius, *Zeitsch. anal. Chem.*, 1876, 15, 295; Hoffmann, *Zeitsch. angew. Chem.*, 1906, 19, 1089.

⁶ Denigès, *Ann. Chim. anal.*, 1915, 20, 59.

rapidly becomes crystalline and under the microscope consists of small clusters.

Small quantities of selenium in solution may be detected by the test described by Meunier,¹ which is similar to Marsh's test for arsenic. If there is a relatively large amount of selenium present it is readily detected by its red colour, but if the amount of the element be small the deposit closely resembles that of arsenic, and in this case the following process may be adopted to detect the selenium. A current of hydrogen sulphide is passed into the hot solution containing a little sulphurous acid. The precipitate of finely divided sulphur carries down with it any selenium present and arsenic as arsenious sulphide, and it is clotted by stirring. In the presence of selenium the clots are brown; they may be dried and the sulphur and selenium separated by careful sublimation in a closed tube.

Selenium may also be detected in solution by the addition of a little concentrated sulphuric acid and a few small crystals of hydrazine sulphate. On warming, a red coloration or precipitate indicates the presence of the element,² the reaction being sensitive to 5 mgms. of selenium per litre.

To detect selenious acid in the presence of selenic acid,³ 3 c.c. of the solution may be treated with 5 c.c. of concentrated sulphuric acid, a little sodium sulphite added and the mixture boiled. A red coloration indicates the presence of selenious acid. After filtering off any precipitate, 3 c.c. of concentrated hydrochloric acid and more solid sodium sulphite are added and the solution again boiled; a red coloration or precipitate then indicates selenic acid. The sensitiveness of this test is the same as for the preceding test.

The presence of selenium in sulphuric acid may be detected by distilling with a few c.c. of bromine water containing potassium bromide. The distillate, collected in a few c.c. of concentrated hydrochloric acid and saturated with sulphur dioxide and cooled, gives a precipitate of the element if present.⁴ By this means 1 part of selenium in 10⁷ parts of acid can be detected. Another method depends upon the addition of aspidospermine, which gives an intense violet colour when selenium is present.⁵ This test is less satisfactory than the preceding one, however, since the colour varies with acid concentration and time of heating. Moreover, although pure sulphuric acid gives no coloration with aspidospermine, if an oxidising agent such as potassium chlorate or lead dioxide be present, a rose-red coloration develops. A process that will detect 0.0005 per cent. of selenious acid in sulphuric acid involves the use of either morphine or codeine.⁶ As an example of the test, mix 1 c.c. of a 0.1 per cent. aqueous solution of selenious acid with 200 c.c. of pure concentrated sulphuric acid; 10 c.c. of this mixture will with 0.1 gram of codeine phosphate after one minute produce a distinct green coloration and after fifteen minutes a bluish-green colour. Smaller quantities of the selenious acid mixture will produce the same colour phenomena.

¹ Meunier, *Compt. rend.*, 1916, 163, 332.

² Müller, *Zeitsch. physikal. Chem.*, 1922, 100, 346.

³ Müller, *loc. cit.*

⁴ Wells, *J. Washington Acad. Sci.*, 1928, 18, 127.

⁵ Palet, *Anal. Soc. Quim. Argentina*, 1917, 5, 121.

⁶ Schmidt, *Arch. Pharm.*, 1914, 252, 161; Reichinstein, *Trans. Inst. Pure Chem. Reagents (Russia)*, 1927, 6, 27; *Chem. Zentr.*, 1928, 1, 230.

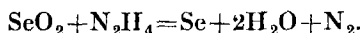
Against a white surface this colour reaction may be observed even with a 0.00001 per cent. concentration of selenious acid. The reaction is more sensitive with sulphuric acid above 75 per cent. concentration than with dilute acid. The test is not applicable if the sulphuric acid contains iron. Tellurous acid retards the reaction.¹

Still another method for the detection of small quantities of selenious acid consists in adding sodium hydrosulphite, $\text{Na}_2\text{S}_2\text{O}_4$, to the solution,² which is then neutralised with solid sodium carbonate. The presence of the least trace of selenium causes a red coloration due to the colloidal element.

A colorimetric method³ for the detection and estimation of small quantities of selenious acid, which is sensitive to 0.002 per cent., may be carried out as follows: Into two cylinders are put, respectively, 5 c.c. of the solution to be tested and 5 c.c. of a solution of selenious acid of approximately the same strength. 70 c.c. of water are added to each and also a drop of gum arabic; then 5 c.c. of 5 per cent. hydrochloric acid solution and the whole diluted to 99 c.c. 1 c.c. of a solution of potassium iodide is added to each tube and the contents vigorously stirred. The respective colorations (due to iodine and colloidal selenium) are compared after five minutes in a Krüss colorimeter.

Estimation.—The general method for the estimation of selenium consists in oxidising it to selenious acid and subsequently precipitating it as the element by means of a suitable reducing agent, such as sulphurous acid or hydrazine hydrate. The red selenium produced is converted to the more granular grey variety by boiling, and can then be filtered on to a Gooch crucible, dried at 105°C . and weighed.

Hydrazine hydrochloride or sulphate as the reducing agent is also said to give good results,⁴ when the volume of nitrogen evolved is measured:



The gas is collected over boiled water. The evolution is soon complete and stops abruptly, so that the end of the reaction is clearly seen. This method is available for small quantities of selenium, since 1 gram of the dioxide yields 201.83 c.c. of nitrogen at N.T.P.⁵

Hypophosphorous acid in slightly alkaline solution reduces selenic acid quantitatively to the element, which can be separated, collected, dried and weighed. If the selenium is originally in a high stage of oxidation it should first be reduced by boiling with hydrochloric acid until no more chlorine is evolved.⁶

A rapid method of dealing with the precipitated selenium is to wash it and dissolve it in a cold saturated solution of sodium sulphide. The red colloidal solution obtained can be titrated with a standard potassium cyanide solution,⁷ the end-point being marked by a change of colour from red to yellow:



¹ For the application of the test to decolorised bottle glass, see Bowmaker and Caulwood, *J. Soc. Glass Technology*, 1927, 11, 386.

² Meyer and Jannet, *Zeitsch. anal. Chem.*, 1913, 52, 534.

³ Meyer and von Garn, *ibid.*, 1913, 53, 29.

⁴ Pellini and Spelta, *Gazzetta*, 1903, 33, ii., 89.

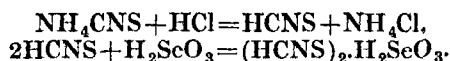
⁵ For a modification of this method, see Gutbier and Engeroff, *Zeitsch. anal. Chem.*, 1915, 54, 193.

⁶ Gutbier and Rohn, *Zeitsch. anorg. Chem.*, 1903, 34, 448.

⁷ Benesch, *Chem. Zeit.*, 1928, 52, 878.

Selenious acid readily decomposes potassium permanganate, but analytical results are untrustworthy in the presence of more than a limited quantity of sulphuric acid.¹ The oxidation should be carried out at 50° C., a known quantity of 0.1*N* potassium permanganate being used and the excess determined either by means of standard oxalic acid solution or by electrometric titration with ferrous sulphate. In the presence of tellurium, the latter is also oxidised and should be determined in a separate sample by oxidation with potassium dichromate, which does not oxidise the selenium, and the necessary deduction can then be made.²

By the interaction of a thiocyanate and selenious acid in the presence of hydrochloric acid, thiocyanoselenious acid is formed :



This compound is rapidly decomposed by hot water with the deposition of amorphous selenium, which may be filtered off, dried and weighed.³ This amorphous selenium, however, may contain some admixed sulphur, which should be estimated by treatment with aqua regia and precipitation with barium chloride, and then allowed for.⁴

A method involving electrometric titration depends on the volumetric reduction of selenious acid to selenium by means of titanium sulphate. The method is rapid and accurate⁵ if the solution is in cold concentrated hydrochloric acid saturated with sodium chloride. The presence of the latter is important, for it ensures rapid and uniform coagulation of the selenium hydrosol and increases the sharpness in the change of voltage at the end-point. The use of the hydrochloric acid in the cold eliminates the otherwise almost inevitable loss of selenium by volatilisation. Under these conditions any tellurium which may be present is unreduced and only has the effect of modifying the nature of the end-point.⁶

Estimation of Selenium in Organic Compounds.—A trustworthy method consists in oxidising the substance with fuming nitric acid, refluxing with concentrated hydrochloric acid until the nitrous fumes disappear and then precipitating the selenium with sodium sulphite.⁷

The Carius method can also be adapted for the estimation of selenium in organic compounds.⁸ About 0.2 gram of the substance is treated with nitric acid (sp. gr. = 1.4) and about 0.5 gram of silver nitrate. The contents of the tube are transferred to a basin, evaporated to dryness, washed with alcohol and then dissolved in 20 per cent. nitric acid.

¹ Gooch and Clemons, *Zeitsch. anorg. Chem.*, 1895, 9, 360; Marino, *ibid.*, 1909, 65, 32; Moser and Prinz, *Zeitsch. anal. Chem.*, 1918, 57, 277.

² Schrenk and Browning, *J. Amer. Chem. Soc.*, 1926, 48, 2550; Littman, *Chem. Zeit.*, 1927, 51, 323.

³ Ivanoff, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 661.

⁴ For a method involving the use of silver, see Perkins, *Zeitsch. anorg. Chem.*, 1910, 67, 361.

⁵ Willard and Fenwick, *J. Amer. Chem. Soc.*, 1923, 45, 933. See also Tomiček, *Bull. Soc. chim.*, 1927, [iv.], 41, 1389.

⁶ For an electro-analytical method for the estimation of small quantities of selenious acid, see Müller, *Zeitsch. physikal. Chem.*, 1922, 100, 346.

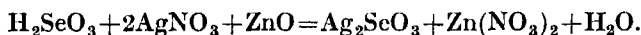
⁷ Bauer and Michaelis, *Ber.*, 1915, 48, 607, 873.

⁸ Frerichs, *Arch. Pharm.*, 1902, 240, 656.

This solution is then diluted and titrated with standard potassium thiocyanate solution, using ammonium iron alum as indicator.¹

Another method² consists in burning the organic substance in oxygen in the presence of platinum as catalyst; the selenium is oxidised to selenious acid, which is titrated with *N*/100 sodium hydroxide. If sulphur is present in addition to selenium the mixed sulphuric and selenious acids obtained are titrated, the sulphuric acid being afterwards estimated separately as barium sulphate. If, however, the substance contains either nitrogen or a halogen, titration is useless. The selenious acid should, in this case, be reduced by means of sodium sulphite in the presence of a large amount of hydrochloric acid. The selenium thus formed may be weighed.

In the absence of the halogens the selenium may be oxidised to selenious acid by heating with nitric acid in a Carius tube at 240° to 300° C. The resulting liquid is nearly neutralised, excess of zinc oxide added, and the mixture titrated with silver nitrate using chromate as external indicator:³



A blank titration against a suspension of zinc oxide is necessary.⁴

*Estimation of Selenium in Sulphide Minerals.*⁵—In various sulphite-cellulose manufactories difficulties have occurred which have been traced to the presence of selenium in the pyrites used for burning. Part of the selenium remains in the burnt pyrites and part volatilises with the sulphur dioxide. 20 to 30 grams of pyrites are dissolved in hydrochloric acid (dens.=1.19) and potassium chlorate. Zinc is added to reduce the iron to the ferrous condition; more hydrochloric acid is then added, the solution boiled and stannous chloride added to precipitate selenium. Since the selenium may contain arsenic, it is collected on an asbestos filter, dissolved in potassium cyanide and reprecipitated using hydrogen chloride and sulphur dioxide. The element may then be estimated by the iodometric method described below. In order to determine the relative proportion of volatile to non-volatile selenium, the pyrites may be roasted in a current of oxygen. After this treatment the contents of the tube are dissolved in warm potassium cyanide and the selenium reprecipitated and estimated in the ordinary way.

In the iodometric method for the quantitative estimation of small quantities of selenium in pyrites use is made of the reaction



The dioxide should be dissolved in water and the solution diluted largely. A few drops of hydrochloric acid are added and the whole heated on a water-bath. A stream of carbon dioxide is introduced to replace the air and solid potassium iodide added. The flask should be corked, its

¹ See also method described by Lyons and Schinn, *J. Amer. Chem. Soc.*, 1902, 24, 1087.

² Wrede, *Zeitsch. physiol. Chem.*, 1920, 109, 272.

³ Bradt and Lyons, *J. Amer. Chem. Soc.*, 1926, 48, 2642.

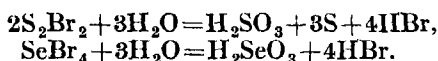
⁴ For a method involving combustion in a Parr bomb, see Shaw and Reid, *ibid.*, 1927, 49, 2330.

⁵ Klason and Mellquist, *Arkiv. Kem. Min. Geol.*, 1911, 4, No. 18, 1; 1912, 4, No. 29, 1-10; 1913, 4, No. 34, 1. See also Schmidt, *Metall und Erz*, 1925, 22, 511; *Chem. Zentr.*, 1926, I., 739. For the separation of As from Se, see Fridli, *Pharm. Zentr.*, 1926, 67, 369.

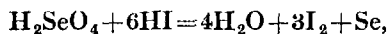
contents shaken and kept in the dark for about an hour, when the liberated iodine may be titrated with standard thiosulphate.¹ Care must be taken that the hydrochloric acid used is free from chlorine, and that the potassium iodide contains no iodate. The method is trustworthy if the amount of iodide used is four times the theoretical quantity,² and it is applicable to solutions of selenious acid in general. The degree of accuracy is improved by the addition of carbon disulphide before the liberation of iodine. The latter then completely dissolves in the organic solvent and is not partly adsorbed on the precipitated selenium; hence the subsequent titration with thiosulphate is more easily accomplished.³

The detection and estimation of selenium in the mother-liquors from the preparation of sulphite-cellulose is rendered difficult by the colour of these liquors, due to the organic substances present. The presence of the element is indicated by the fact that a red deposit is formed on the sides of the combustion tube when the organic matter is being burnt off. Estimation may be carried out by evaporating the liquor until all the free sulphur dioxide has been evolved, acidifying with hydrochloric acid and boiling to remove the last traces of sulphur dioxide. After allowing to stand in a warm place for a few days the selenium settles to the bottom of the container and may be estimated as described.⁴

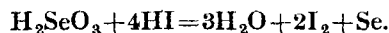
The method of estimation of selenium in sulphur depends upon the fact that sulphur and selenium bromides are decomposed by water according to the equations:



The reaction with the selenium compound is much more rapid than that with the sulphur compound. Some of the selenious acid becomes oxidised to selenic acid. When these selenium acids are treated with excess of hydriodic acid they become reduced to selenium:



and



The selenium formed is collected, dried at 100° C. and weighed.⁵

¹ Muthmann and Schafer, *Ber.*, 1893, 26, 1008.

² Moser and Prinz, *Zeitsch. anal. Chem.*, 1918, 57, 277.

³ Berg and Teitelbaum, *Chem. Zeit.*, 1928, 52, 142.

⁴ Klason and Mellquist, *Arkiv. Kem. Min. Geol.*, 1913, 4, No 34, 1.

⁵ Smith, *J. Ind. Eng. Chem.*, 1915, 7, 849.

CHAPTER V.

COMPOUNDS OF SELENIUM.

THE compounds of selenium are in large measure analogous to those of sulphur, but whereas the latter element exists principally in the bivalent or sexavalent condition, selenium is quadrivalent in its most stable compounds (see p. 304). There are consequently marked differences between the properties of many of the corresponding compounds of the two elements, and selenium is more closely allied to tellurium (see later) than to sulphur.

The ease with which selenium combines with many other elements to form binary compounds has already been mentioned (p. 299). Only one compound with hydrogen is known, but a series of polyselenides of the alkali metals corresponding to the polysulphides has been obtained. Selenium forms a hexafluoride, SeF_6 , but no other hexahalide has been isolated. The tetrahalides are the most stable, and mixed chlorobromides of quadrivalent selenium, $\text{SeCl}_{4-x}\text{Br}_x$, are known. Selenium monochloride, Se_2Cl_2 , and selenium monobromide, Se_2Br_2 , also exist as comparatively stable liquids at ordinary temperatures. No compound of selenium and iodine is known. Selenium oxychloride, SeOCl_2 , and the oxybromide, SeOBr_2 , are extremely reactive and useful compounds.

Only one oxide, the dioxide, SeO_2 , is definitely known (see p. 326). The anhydride of selenic acid, SeO_3 , has resisted all attempts at preparation by methods analogous to those used for sulphur trioxide, and its actual isolation is still unsubstantiated (see p. 331). Selenium dioxide, the product of the combustion of selenium in oxygen, is a hygroscopic crystalline solid. From its solution in water, selenious acid, H_2SeO_3 , may be separated in crystalline form. This acid is more stable than sulphurous acid and is only oxidised to selenic acid by powerful oxidising agents, such as chlorine. It is, however, readily reduced to the element, red amorphous selenium being precipitated, and in this respect selenium compounds generally are somewhat more sensitive towards reducing agents than the corresponding tellurium compounds. Selenic acid may be obtained in the solid state; in solution it resembles sulphuric acid in its chemical properties but is not quite so reactive. The selenates are similar to and often isomorphous with the corresponding sulphates, which they also resemble in the formation of double salts; for example, a series of selenium "alums" has been prepared (see p. 337). There are indications that a perselenic acid may exist (p. 337), but such a compound has not been isolated.

Although selenium does not appear to form a series of acids corresponding with the polythionic acids, several compounds derived from the latter by substitution of selenium for part of the sulphur, for example $\text{H}_2\text{SeS}_2\text{O}_6$, $\text{H}_2\text{Se}_2\text{SO}_6$, etc. (see pp. 339, 340), have been prepared.

Selenium does not combine directly with nitrogen, but a compound of the two elements, selenium nitride, Se_4N_4 , has been obtained by the

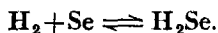
interaction of ammonia and certain halogen derivatives. It is an explosive solid which reacts violently with chlorine and bromine but not with iodine. Nitrosylselenic acid, $\text{NO}_2\cdot\text{SeO}_2\cdot\text{OH}$, has been obtained by the action of nitrogen trioxide on anhydrous selenic acid in the cold.

Selenium resembles sulphur in combining directly with phosphorus to form a number of well-defined compounds (see p. 341). Seleno-phosphates of the type $\text{M}_3\text{PSe}_x\text{O}_{4-x}$ have also been prepared (pp. 342, 343).

SELENIUM AND HYDROGEN.

Hydrogen Selenide, H_2Se .—This compound was discovered in 1817 by J. J. Berzelius as the gaseous product of the interaction of hydrochloric acid and iron selenide or potassium selenide.

Formation and Preparation.—(1) Hydrogen and selenium combine on heating:

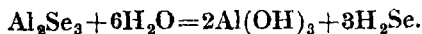


The action begins appreciably near 250°C ., and with rise of temperature there is an increasing percentage of hydrogen selenide in the equilibrium mixture until a maximum (exceeding 50 per cent.) is reached near 570°C ., above which temperature the percentage decreases. On account of this behaviour, selenium heated in one part of a tube containing hydrogen gives a crystalline deposit in the cooler parts of the tube, the apparent sublimation being due to the formation of hydrogen selenide at the higher temperature and its partial decomposition by cooling away from the heated space. If the cooling is effected rapidly it is possible to check the readjustment of the equilibrium.¹ The gas can be purified by cooling in liquid air, when the free hydrogen remains uncondensed.²

(2) Aqueous solutions of selenious acid yield small quantities of hydrogen selenide when submitted to the action of nascent hydrogen.³

(3) Phosphorus pentaselenide, obtained by heating together an intimate mixture of selenium and red phosphorus, when warmed with water gives a steady stream of hydrogen selenide.⁴

(4) From metallic selenides.—Aluminium selenide is easily decomposed, even by water, with formation of hydrogen selenide :⁵



Many metallic selenides yield the gas when treated with dilute mineral acids. For example, when aluminium or magnesium selenide is dropped slowly into the acid a continuous stream of hydrogen selenide is generated, which can be dried by means of phosphorus pentoxide. If required in a high degree of purity, the dried gas can be liquefied, *e.g.* by means of a mixture of ether and solid carbon dioxide, and obtained pure by re-vaporisation.⁶

¹ See Pélabon, *Compt. rend.*, 1893, 116, 1292; 1894, 118, 142; 119, 73; 1897, 124, 360; *Zeitsch. physikal. Chem.*, 1898, 26, 859; Bodenstein, *ibid.*, 1899, 29, 429.

² Hempel and Weber, *Zeitsch. anorg. Chem.*, 1912, 77, 48.

³ Meunier, *Compt. rend.*, 1916, 163, 332.

⁴ Becker and Meyer, *Ber.*, 1904, 37, 2550; Hahn, *J. prakt. Chem.*, 1864, 93, 430; Bogen, *Annalen*, 1862, 124, 57.

⁵ Fonzes-Diacon, *Compt. rend.*, 1900, 130, 1314; also de Forcrand and Fonzes-Diacon, *Ann. Chim. Phys.*, 1902, [vii.], 26, 247.

⁶ Moser and Doctor, *Zeitsch. anorg. Chem.*, 1921, 118, 284.

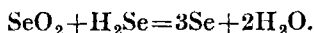
(5) Fairly pure hydrogen selenide can be obtained by heating selenium with several times its weight of resin or paraffin wax, the temperature in the latter case being 335° to 340° C. The organic impurities are easily removed, being almost entirely eliminated at 60° C. A good yield of the gas is obtained.¹

Physical Properties.—Hydrogen selenide is a colourless gas the odour of which at first suggests hydrogen sulphide, but afterwards is unpleasantly pungent, causing headache and affecting the mucous membrane of the nose in such a way as to induce a form of catarrh.

The liquefied substance solidifies at -64° C. and boils at -42° C. under 760 mm. pressure, the critical temperature being $+138^{\circ}$ C.² One litre of the gas at N.T.P. weighs 3.6715 grams. The solubility in water at 4° C. is 3.77 volumes per unit volume of solvent, whilst at 22.5° C. water dissolves 2.70 times its own volume of the gas.³ The gas is also soluble in molten selenium, being freed on solidification.⁴ The combination of hydrogen gas and amorphous selenium is accompanied by an absorption of 16.0 Cals. per gram-molecule of hydrogen selenide produced; with the use of the more stable monoclinic and metallic forms, the values are 17.0 and 17.4 Cals. respectively.⁵

Chemical Properties.—Hydrogen selenide is not decomposed by daylight but it is sensitive to ultra-violet light. In the presence of moisture, oxygen rapidly decomposes the gas, but if the oxygen and the gas are both dry there is no action.⁶ It burns with a blue flame, producing water and selenium or selenium dioxide, according to the supply of oxygen.

When passed over heated iron boride, the gas interacts, forming iron selenide and selenium boride.⁷ With water no stable compound is produced, although the existence of an unstable crystalline hydrate has been observed.⁸ Sulphur dioxide and selenium dioxide oxidise a solution of hydrogen selenide, the product in the latter case being red selenium :⁹



With ammonia, hydrogen selenide reacts at the ordinary temperature with the formation of a white crystalline mass of ammonium selenide,¹⁰ $(\text{NH}_4)_2\text{Se}$; the same compound is produced by passing hydrogen selenide into a concentrated aqueous solution of ammonia at 0° C., the air in the apparatus having been displaced by nitrogen.

The Selenides.—Hydrogen selenide exhibits stronger acidic properties than hydrogen sulphide, and many of the heavy metals may be precipitated as selenides from aqueous solutions of their salts under conditions generally analogous to those required for the precipitation of

¹ Étard and Moissan, *Bull. Soc. chim.*, 1880, [n.], 34, 69; also Wuyts and Stewart, *Bull. de Belg.*, 1909, 23, 9.

² de Forcrand and Fonzes-Diacon, *Compt. rend.*, 1902, 134, 171, 229; also Olszewski, *Phil. Mag.*, 1895, [v.], 39, 188.

³ de Forcrand and Fonzes-Diacon, *loc. cit.*

⁴ Pélabon, *Compt. rend.*, 1893, 116, 1292.

⁵ Rolla, *Atti R. Accad. Lincei*, 1912, [v.], 21, n., 278, 463; also Berthelot, *Compt. rend.*, 1880, 91, 18; 1875, 80, 516; Moissan, *Ber.*, 1879, 12, 2380; Fabre, *Compt. rend.*, 1886, 103, 131.

⁶ Moser and Doctor, *Zeitsch. anorg. Chem.*, 1921, 118, 284.

⁷ Hoffmann, *Chem. Zeit.*, 1911, 35, 713.

⁸ de Forcrand, *Compt. rend.*, 1882, 95, 129; 1902, 34, 229.

⁹ Ditte, *Ber.*, 1876, 9, 1432.

¹⁰ Wendehorst, *Zeitsch. anorg. Chem.*, 1926, 153, 263.

sulphides; manganous selenide may be precipitated from slightly acid solution. The selenides so obtained, however, are usually impure, owing to deposition of the metal or of selenium or the formation of complexes and double salts, and the pure selenides are best prepared by the methods outlined below.

In the wet way selenides are best produced by allowing the solution of the metallic salt to drop slowly into a saturated aqueous solution of hydrogen selenide which is mechanically stirred. In this way the selenide is formed in the presence of excess of hydrogen selenide, no excess of metal ions being at any time present in the solution.¹ The alkali selenides may be obtained by the action of hydrogen selenide on the corresponding carbonates in aqueous solution in an atmosphere of nitrogen,² followed by crystallisation from solution.

The selenides may also be obtained by direct combination of the elements, either by passing selenium vapour over the heated metal in a vacuum or by heating the metal with selenium in a crucible, the reaction being started by means of a magnesium fuse.³ In the case of potassium the reaction is explosive. The compounds may also be obtained by the action of hydrogen selenide on the heated metal,⁴ on the heated metallic chloride or its vapour, preferably in the presence of nitrogen,⁵ or by reduction with hydrogen or carbon of an oxysalt such as a selenite.⁶ Selenides have also been prepared by electrolytic methods.⁷

The selenides of the alkali metals are white when pure, but generally appear pink owing to the presence of free selenium or of polyselenides, as also do the alkali hydroselenides; moreover they readily oxidise in air, with separation of selenium. The selenides of the alkaline earth metals are described as pink, but it is questionable whether they have yet been obtained in a pure condition.

Aluminium and magnesium selenides are very similar light brown powders, unstable in air. Zinc and iron (ferrous) selenides are more stable in air, the zinc compound being citron-yellow and the iron compound black and metallic in appearance.⁸ The latter becomes brown in air owing to oxidation. Ferric selenide is difficult to obtain pure. Cadmium selenide, which is dark brown, is very stable in colour and is used as a pigment. With thallium, selenium is said to form three distinct compounds,⁹ but analyses of these compounds have led to discordant results. The selenides of aluminium, chromium and uranium cannot be prepared in the wet way. Nickel selenide, unlike the sulphide, shows no tendency to form a colloidal solution.

As regards solubility in water, the general behaviour of the selenides is analogous to that of the sulphides. Aqueous solutions of the alkali and alkaline earth selenides gradually undergo oxidation by atmospheric oxygen and selenium separates, generally as the amorphous red variety, but sometimes as the crystalline modification.

¹ Moser and Atynski, *Monatsh.*, 1925, 45, 235.

² Fabre, *Compt. rend.*, 1886, 102, 613.

³ Moser and Doctor, *Zeitsch. anorg. Chem.*, 1921, 118, 284; Fonzes-Diacon, *Compt. rend.*, 1900, 130, 1314, 1710; 131, 556, 704.

⁴ Margottet, *ibid.*, 1877, 84, 1293.

⁵ Fonzes-Diacon, *ibid.*, 1900, 130, 832, 1025, 1131; 131, 556, 704, 895, 1206.

⁶ Fabre, *ibid.*, 1886, 102, 1469.

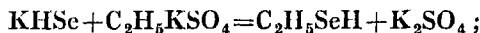
⁷ See Fischer, *Zeitsch. Elektrochem.*, 1925, 31, 286.

⁸ Moser and Doctor, *Zeitsch. anorg. Chem.*, 1921, 118, 284.

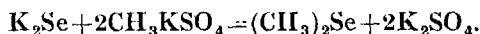
⁹ Rolla, *Atti R. Accad. Lincei*, 1919, [v.], 28, i., 355.

In general, the metal selenides correspond in composition with the sulphides, are much less stable, oxidise quickly in air, and when prepared in the wet way cannot be dried without some decomposition. They are generally deeper in colour than the corresponding sulphides, a fact which is probably associated with the higher atomic weight of selenium.

Organic derivatives of hydrogen selenide of the types R_2SeH and R_2Se are known. These are generally prepared by distilling an alkali hydrogen selenide or alkali selenide with the corresponding alkylsulphate; thus for ethyl selenomercaptan :



and for dimethyl selenide :



With ketones in the presence of concentrated hydrochloric acid, hydrogen selenide yields heavy red oils, which decompose on distillation.¹

Polyselenides of the alkali metals, of the type M_2Se_x , where x may be as many as 5, are known,² but although organic derivatives such as benzyl diselenide $(C_7H_7)_2Se_2$ are stable,³ no hydrogen diselenide analogous to the sulphur and oxygen compounds has been obtained.

A *thioselenide* of composition $Na_2SeS_2 \cdot 5H_2O$ has been prepared.⁴

COMPOUNDS OF SELENIUM WITH THE HALOGENS.

Selenium Fluorides.—Two fluorides of selenium have been described, the *hexafluoride*, SeF_6 , and the *tetrafluoride*, SeF_4 . The former was obtained as a stable gas by the action of fluorine on selenium at $78^\circ C$.⁵ Its boiling-point, melting-point and critical temperature are $-34.5^\circ C$. (in a sealed tube), $-39^\circ C$. and $+72^\circ C$., respectively. The vapour density, 97.23, agrees with the formula SeF_6 .⁶ The gas does not attack glass.

Using a copper containing-vessel for the selenium, Lebeau⁷ obtained a colourless liquid which he analysed and concluded to be selenium tetrafluoride. By the same method, however, Lebeau later obtained a gaseous product the composition of which approximated to SeF_6 but which contained selenium in slight excess of the theoretical amount. Doubt was therefore expressed as to the exact nature of these products, and Prideaux⁸ has shown that the liquid product described by Lebeau somewhat resembles in properties the oxyfluoride $SeOF_2$, or the mixture $SeO_2 + 2HF$. The existence of the hexafluoride was subsequently acknowledged by Lebeau,⁹ and that of the tetrafluoride has recently

¹ Lyons and Bradt, *Ber.*, 1927, 60, [B], 824. See also Shaw and Reid, *J. Amer. Chem. Soc.*, 1926, 48, 520. For the formation of magnesium bromo-derivatives, see Mingoia, *Gazzetta*, 1926, 56, 835.

² Bergstrom, *J. Amer. Chem. Soc.*, 1926, 48, 146.

³ Jackson, *Ber.*, 1874, 7, 1277.

⁴ Prideaux, *Trans. Chem. Soc.*, 1906, 89, 316.

⁵ Ramsay, *Compt. rend.*, 1907, 144, 1196.

⁶ Lebeau, *ibid.*, 1907, 144, 1042. See also Moissan, *Ann. Chim. Phys.*, 1891, [vi.], 24, 214.

⁷ Prideaux and Cox, *J. Chem. Soc.*, 1928, p 1603.

⁸ Lebeau, *Compt. rend.*, 1907, 145, 190.

⁹ Messinger, *ibid.*, 1897, 30, 805.

been established by Prideaux,¹ who has prepared it by the interaction of selenium tetrachloride and silver fluoride. A mixture of these compounds (1 part SeCl_4 to 4–5 parts AgF) was heated in a platinum bottle to 50° to 60° C. The reaction proceeded vigorously and selenium tetrafluoride distilled over as a colourless fuming liquid of density 2.77 and boiling-point 98° C. It could be readily condensed to a solid, which melted at -13.2° C. The liquid readily attacked glass, was hydrolysed by water with formation of selenious and hydrofluoric acids, heat being evolved, and reacted with red phosphorus, gaseous fluorides of phosphorus, selenium and selenium dioxide being produced. It should be observed that the samples of tetrafluoride examined by Prideaux contained some oxyfluoride (see p. 320) and the latter reacts in a similar manner towards the reagents mentioned, as also to some extent does the mixture of selenium dioxide and hydrofluoric acid, $\text{SeO}_2 + 4\text{HF}$. Further investigation is therefore desirable.

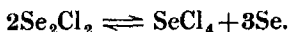
Selenium Monochloride, Se_2Cl_2 .—This chloride is most easily obtained by the action of chlorine on heated selenium, but it is always accompanied by a certain quantity of the more stable tetrachloride which, however, is less volatile.² It may be prepared by saturating with chlorine a suspension of selenium or a selenium mineral in carbon tetrachloride.³ The selenium monochloride is soluble in carbon tetrachloride, whilst the chlorides of other elements present are insoluble. The monochloride is therefore obtained by evaporation of the solvent after filtration.

The chlorides of certain non-metals such as phosphorus have a similar action on selenium, possibly on account of previous dissociation with formation of chlorine.⁴

In some commercial acids selenium is present in the form of the monochloride, produced when seleniferous sulphuric acid is heated with salt. On the addition of ferric chloride, the monochloride gradually separates.⁵

A solution of selenium in fuming sulphuric acid gives a gradual separation of the monochloride on the addition of hydrogen chloride.⁶

Selenium monochloride is a clear reddish-brown liquid of density (D_{40}^{25}) 2.7741, and can be condensed to a solid of melting-point -85° C.⁷ Its odour somewhat resembles that of sulphur monochloride. The liquid has a refractive index of 1.59617 at 25° C., and its specific conductance is 5.12×10^{-7} mho. On vaporisation it undergoes partial dissociation. Boiling commences at 145° C., the yellowish-brown vapour containing the tetrachloride and a residue of selenium being obtained in the retort:⁸



¹ Prideaux and Cox, *loc. cit.*

² See Beckmann, *Zeitsch. anorg. Chem.*, 1913, 84, 103; 1909, 63, 63; *Zeitsch. physikal. Chem.*, 1910, 70, 1.

³ Lenher, *J. Amer. Chem. Soc.*, 1920, 42, 2498.

⁴ Michaelis, *Jahresber. Techn.*, 1870, [ii.], 6, 460.

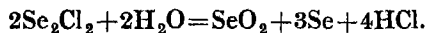
⁵ Moles and de Rubies, *Anal. Fis. Quim.*, 1913, 11, 73.

⁶ Drivers and Shimosé, *Trans. Chem. Soc.*, 1884, 45, 198. For a modification of this method, see Bauser, Gilson and Pope, *ibid.*, 1920, 117, 1453.

⁷ Lenher and Kao, *J. Amer. Chem. Soc.*, 1926, 48, 1550.

⁸ Beckmann, *Zeitsch. physikal. Chem.*, 1910, 70, 1; also Ramsay, *Bull. Soc. chim.*, 1890, [iii.], 3, 783. For the absorption spectrum of selenium monochloride vapour, see Gernez, *Compt. rend.*, 1872, 74, 1190.

The monochloride is soluble in various inert organic liquids, more particularly in benzene, chloroform, carbon tetrachloride and carbon disulphide, without undergoing chemical change. It is an exothermic compound, its heat of formation from gaseous chlorine and the amorphous modification of selenium being 22.1 Cals.¹ Water causes a gradual decomposition of the chloride, selenium dioxide and selenium being formed : ²



Selenium monochloride behaves as a strong chlorinating agent towards metals, metallic selenides and hydrocarbons.³ Phosphorus displaces selenium from the chloride with formation of phosphorus trichloride.⁴ Chlorine converts it into the tetrachloride.

The action of liquid ammonia on selenium monochloride is exceedingly vigorous and results in the deposition of red selenium. The monochloride in ether solution, however, yields with liquid ammonia a pale brown amorphous compound of formula Se_2NCl .⁵

The constitution of selenium monochloride is uncertain ; it may be represented by $\text{Se} : \text{Se} \begin{cases} \text{Cl} \\ \text{Cl} \end{cases}$ or $\text{Cl}-\text{Se}-\text{Se}-\text{Cl}$; that the molecular weight

is in accordance with this formula has been demonstrated by cryoscopic investigation in solution in ethylene dibromide.⁶

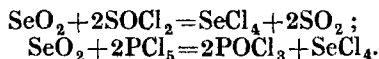
Selenium Tetrachloride, SeCl_4 .—This may be obtained as follows :

(1) By the action of excess of chlorine on selenium or on selenium monochloride in carbon tetrachloride solution ; the tetrachloride is insoluble and precipitates as rapidly as it is formed as a white powder :



Baudrimont ⁷ obtained the tetrachloride by the action of phosphorus pentachloride vapour on lead selenide.

(2) By various methods from selenium dioxide ; for example, by the action of hydrogen chloride, thionyl chloride or phosphorus pentachloride. The last-named is perhaps the most convenient chlorinating agent. A mixture of the pentachloride and the dioxide is heated until chemical change causes it to solidify. Phosphorus oxychloride can be distilled off with the aid of a current of carbon dioxide and the residual selenium tetrachloride purified by sublimation.⁸



The disappearance of selenium during the evaporation of a solution of selenium dioxide in concentrated hydrochloric acid is probably due to the formation of the tetrachloride.⁹

¹ Thomsen and Burke, *Thermochemistry* (Longmans, Green & Co., 1908), p. 250.

² Sacc, *Ann. Chim. Phys.*, 1848, [iii.], 23, 124.

³ Lenher and Kao, *loc. cit.*

⁴ Baudrimont, *Ann. Chim. Phys.*, 1864, [iv.], 2, 9, 37.

⁵ Strecker and Claus, *Ber.*, 1923, 56, [B], 362.

⁶ Beckmann, *Zeitsch. anorg. Chem.*, 1909, 63, 63.

⁷ Baudrimont, *loc. cit.*

⁸ Chabré, *Bull. Soc. chim.*, 1890, [iii.], 3, 245, 677 ; 4, 178.

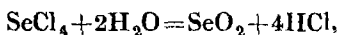
⁹ Meyer, *Zeitsch. anal. Chem.*, 1914, 53, 145.

(3) Selenates, on distillation with sulphuric acid and sodium chloride, yield a mixture of selenium tetrachloride and chlorine; anhydrous selenic acid also gives an excellent yield of selenium tetrachloride on treatment with acetyl chloride at 0°C .¹

Selenium tetrachloride is a colourless solid which on heating vaporises without melting. Sublimation in an atmosphere of chlorine is therefore a convenient method of purification. The density of the vapour (which is yellow in colour) indicates that dissociation occurs to a considerable extent above 200°C ., although below this temperature the results are in accordance with the formula SeCl_4 .² The products of dissociation are probably the lower chloride and chlorine. There are indications that at higher temperatures (500°C .) the dichloride, SeCl_2 , is formed. When the tetrachloride is heated in a sealed tube with selenium, the monochloride is produced.³

The tetrachloride may be purified by recrystallisation from phosphorus oxychloride, from which it separates as cubical crystals. It is practically insoluble in carbon disulphide, which can therefore be used to remove any monochloride present. The heat of formation of the tetrachloride from chlorine and amorphous selenium is 46.1 Calories.⁴

Water decomposes the tetrachloride, forming the dioxide,

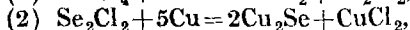
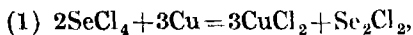


but if the quantity of water is very small, the oxychloride, SeOCl_2 , is obtained.⁵

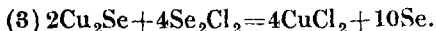
The action of dry ammonia on a suspension of the tetrachloride in carbon disulphide gives ammonium chloride and the very explosive orange-yellow amorphous solid nitrogen selenide, N_4Se_4 .⁶

Excess of phosphorus displaces the selenium from the tetrachloride with the formation of phosphorus trichloride.⁷

When copper is heated with the tetrachloride at 105°C . in an evacuated tube, the reaction proceeds according to the equations:⁸



and, if the chloride is present in excess,



Selenium Monobromide, Se_2Br_2 .—This is produced together with the tetrabromide by the action of boiling bromine on selenium.⁹ The reaction, which is accompanied by considerable heat evolution, may be moderated by dissolving the bromine in carbon disulphide.¹⁰ The substance can also be produced by treating the tetrabromide with selenium at the ordinary temperature.¹¹

¹ Lamb, *Amer. Chem. J.*, 1903, 30, 209.

² Evans and Ramsay, *Trans. Chem. Soc.*, 1884, 45, 65. See also Simons, *J. Amer. Chem. Soc.*, 1930, 52, 3483.

³ Michaelis, *Jahresber. Techn.*, 1870, [ii.], 6, 460.

⁴ Thomsen and Burke, *Thermochemistry* (Longmans, Green & Co., 1908), p. 234.

⁵ Weber, *Ann. Chim. Phys.*, 1859, 108, 615.

⁶ Verneuil, *Bull. Soc. chim.*, 1882, [2], 38, 548; *Ber.*, 1883, 16, 219; Berthelot and Vieille, *Compt. rend.*, 1883, 96, 213.

⁷ Bandrimont, *Ann. Chim. Phys.*, 1864, [iv.], 2, 9, 37.

⁸ Taylor, Prideaux and Pool, *J. Amer. Chem. Soc.*, 1926, 48, 2129.

⁹ Beckmann, *Zeitsch. physikal. Chem.*, 1910, 70, 1.

¹⁰ Schneider, *Ann. Phys. Chem.*, 1866, [ii.], 128, 327.

¹¹ Schneider, *loc. cit.*

It is a very deep red liquid having a density of 3.60 at 15° C.; its odour is unpleasant. It is soluble in carbon disulphide and in chloroform and is, in its turn, a solvent for selenium. When heated, partial decomposition occurs, with formation of bromine and the tetrabromide, distillation taking place at 225° C.

The action of water on selenium monobromide is analogous to the action on the corresponding chlorine compound, selenium and selenium dioxide being formed.

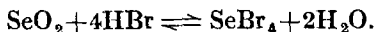
Combination with bromine readily occurs, with production of the tetrabromide.

Selenium monobromide reacts with gaseous ammonia in a similar way to the corresponding chloride. With liquid ammonia in the presence of ether, it gives the compound $\text{Se}_2\text{N}_2\text{Br}$.¹

From the fact that on reacting with organo-magnesium compounds selenium monobromide gives rise to organic substances containing a chain linking, $-\text{Se}-\text{Se}-$, it is probable that the constitution is to be represented by $\text{Br}-\text{Se}-\text{Se}-\text{Br}$.²

Selenium Tetrabromide, SeBr_4 , is formed by the action of excess of bromine on selenium or on selenium monobromide, the latter preferably being in solution in carbon disulphide, in order to moderate the vigour of the process.³

When selenium dioxide is dissolved in aqueous hydrobromic acid, selenium tetrabromide is also formed :



Its presence may be shown by the separation of potassium selenibromide, K_2SeBr_6 , on addition of concentrated potassium bromide solution.

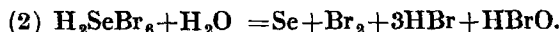
Selenium tetrabromide is a reddish-brown crystalline powder which decomposes to some extent on warming, giving bromine and the monobromide, but much sublimes unchanged.

With sufficient water the tetrabromide is decomposed into the dioxide and hydrobromic acid. Carbon disulphide and chloroform dissolve it to a slight extent.

With the alkali bromides and alkyl ammonium bromides selenium tetrabromide can form crystalline additive compounds of the type M_2SeBr_6 , termed selenibromides. Indeed, by the action of bromine on finely divided selenium in the presence of concentrated hydrobromic acid, a solution is obtained⁴ which gradually deposits deep red crystals of hydrogen selenibromide, H_2SeBr_6 . The solution of this body in hydrobromic acid on dilution with water undergoes decomposition with liberation of colloidal selenium. Two reactions probably occur concurrently :



and



¹ Strecker and Claus, *Ber.*, 1923, 56, [B], 362.

² Pieroni and Coli, *Gazzetta*, 1914, 44, ii., 349; Pieroni and Balduzzi, *ibid.*, 1915, 45, ii., 106.

³ Schneider, *Ann. Phys. Chem.*, 1866, [ii.], 128, 327.

⁴ Norris and Mommers, *J. Amer. Chem. Soc.*, 1900, 23, 486; Gutbier and others, *J. prakt. Chem.*, 1912, [ii.], 85, 321; *Kolloid-Zeitsch.*, 1914, 15, 193, 210.

The *potassium* and *ammonium selenibromides* have been prepared by dissolving selenium dioxide in hydrobromic acid and adding either potassium or ammonium bromide. The selenibromides are orange-red in colour and are decomposed by water into selenious acid, hydrogen bromide and the alkali bromide, yielding colourless solutions.¹

Selenium tetrabromide and sulphur trioxide yield the additive compound $\text{SeBr}_4 \cdot 2\text{SO}_3$ in the form of bright yellow needles which at 170°C. form the yellow compound $\text{SeOBr}_2 \cdot \text{SO}_3$.²

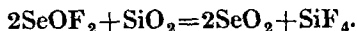
Selenium Trichlorobromide, SeCl_3Br , Selenium Dichlorodibromide, SeCl_2Br_2 , and Selenium Chlorotribromide, SeClBr_3 , have been described as yellow crystalline compounds, the first being obtained by the action of chlorine on selenium monobromide and the last by the action of bromine on selenium monochloride, while the intermediate body has been obtained by the action of chlorine on a mixture of selenium tetrabromide and monobromide.³

Compounds with Iodine.—The freezing-point and vapour pressure curves for mixtures of selenium and iodine give no indication of any combination between these two elements and no definite compounds have been obtained by any chemical process.⁴

By the addition of iodine to a solution of phosphorus selenide, P_4Se_3 , in carbon disulphide Mai⁵ has obtained as a solid substance, *tetraphosphorus di-iodide triselenide*, $\text{P}_4\text{I}_2\text{Se}_3$, which on rapid heating melts at 154° to 155°C.

Selenium Oxyhalides.

Selenium Oxyfluoride, SeOF_2 .—When dry hydrogen fluoride vapour is passed over selenium dioxide, the former is rapidly absorbed, the product liquefying and becoming warm.⁶ From this liquid Prideaux has isolated a product approximating to the composition $\text{SeO}_2 \cdot 5\text{HF}$, but a definite oxyfluoride does not appear to be obtainable by this method. The oxyfluoride, SeOF_2 , may be prepared⁷ by passing selenium oxychloride vapour over silver fluoride at 140° to 200°C. ; the reaction begins suddenly, and copious fumes are evolved which may be condensed to a colourless liquid of density 2.67 and boiling-point 124°C. This solidifies to an ice-like mass which melts at 4.6°C. Glass is readily attacked by the liquid or vapour, a white deposit of selenium dioxide being formed :



The reaction with red phosphorus is violent and accompanied by inflammation, the products being similar to those described with the tetrafluoride. The oxyfluoride is hydrolysed by water with evolution of heat.

Selenyl Chloride, Selenium Oxychloride, SeOCl_2 , may be prepared in the following ways :

¹ Muthmann and Schäfer, *Ber.*, 1893, 26, 1008.

² Prandtl and Borinski, *Zeitsch. anorg. Chem.*, 1909, 62, 237.

³ Evans and Ramsay, *Trans. Chem. Soc.*, 1884, 45, 62.

⁴ Pellini and Pedrina, *Atti R. Accad. Lincei*, 1908, [v.], 17, 78; Wright, *Trans. Chem. Soc.*, 1915, 107, 1527.

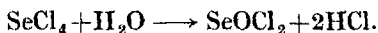
⁵ Mai, *Ber.*, 1927, 60, [B], 2222.

⁶ Ditte, *Compt. rend.*, 1876, 83, 225; Prideaux and Millott, *J. Chem. Soc.*, 1928, p. 187.

⁷ Prideaux and Cox, *ibid.*, 1928, p. 739.

(1) By adding the calculated amount of dry selenium dioxide to selenium tetrachloride suspended in carbon tetrachloride. The oxychloride formed in the cold dissolves in the carbon tetrachloride, from which it may be obtained by distillation. Carbon tetrachloride distils at 76° to 77° C., while the selenium oxychloride distils over at 176.4° C.¹

(2) By the partial hydrolysis of selenium tetrachloride :

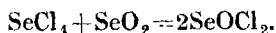


The tetrachloride may either be used alone or suspended in carbon tetrachloride.²

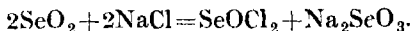
(3) When selenium dioxide is brought into contact with dry hydrogen chloride at low temperatures, an amber-coloured liquid is obtained having the formula $\text{SeO}_2 \cdot 2\text{HCl}$ (see p. 325).³ By dehydration of this compound, using phosphorus pentoxide, calcium chloride or other similar dehydrating agent, selenium oxychloride is formed and can be separated by distillation.

This reaction may also be effected by mixing together the selenium dioxide and the dehydrating agent, passing in hydrogen chloride in the cold and then distilling off the oxychloride.⁴

(4) When a mixture of selenium dioxide and selenium tetrachloride is heated in a sealed tube, selenium oxychloride is formed :⁵



(5) Selenium oxychloride is also formed when selenium dioxide is heated with sodium chloride :⁶



Selenium oxychloride is a nearly colourless liquid having a boiling-point of 176.4° C. at 726 mm. Its melting-point is 10.8° C.⁷ At 20° C. it has a refractive index of 1.6516. The specific conductivity of the dry liquid at 25° C. is $8.2 \cdot 0 \text{ } (\pm 0.3) \times 10^{-5}$ mho. The oxychloride is, however, extremely hygroscopic, and the presence of traces of water causes a considerable increase in the electrical conductivity. The presence of the merest trace of water can be shown⁸ by sealing up a sample of the oxychloride with cobalt carbonate which has been dried at 200° C. for three hours ; a blue colour gradually develops if moisture is present.

Selenium oxychloride absorbs all light up to a wave-length of $4050\mu\mu$. It is miscible with chloroform, carbon disulphide and benzene without chemical change. It is also soluble in carbon tetrachloride, but after a time reaction takes place with formation of selenium tetrachloride and carbonyl chloride.¹⁰ At the ordinary temperatures selenium oxychloride is not miscible with the paraffin hydrocarbons,

¹ Lenher, *J. Amer. Chem. Soc.*, 1920, 42, 2498.

² Lenher, *loc. cit.*

³ Ditte, *Ann. Chim. Phys.*, 1877, [5], 10, 82.

⁴ Lenher, *loc. cit.*

⁵ Cameron and Macallan, *Chem. News*, 1889, 59, 219 ; Ray, *J. Amer. Chem. Soc.*, 1923, 45, 2090.

⁶ Cameron and Macallan, *loc. cit.*

⁷ Lenher, Smith and Town, *J. Physical Chem.*, 1922, 26, 156.

⁸ Julien, *J. Amer. Chem. Soc.*, 1925, 47, 1799.

⁹ Lenher, *ibid.*, 1922, 44, 1664.

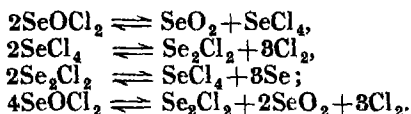
¹⁰ Lenher, *loc. cit.*

SULPHUR, SELENIUM, AND TELLURIUM.

but at higher temperatures (150° to 160° C.) it is completely miscible with higher paraffins such as vaseline.

Selenium oxychloride, when distilled under reduced pressures, has a light straw colour, but when distilled under atmospheric pressure it decomposes slightly and becomes reddish-brown; this decomposition reverses to some extent on cooling.

At temperatures between 265° and 290° C. there is a small amount of dissociation, since the mean value of the molecular weight over this range of temperature is 151.4 ($\text{SeOCl}_2 = 166.12$). The following decompositions occur to a small extent at or near the boiling-point under atmospheric pressure: ¹



The vapour pressure of selenium oxychloride has been determined at temperatures between 84.3° and 117.2° C. It can be expressed by the formula ²

$$\log P = 5.8503 + 0.000219T - 830.9/(T - 178),$$

where P = pressure in mm. of mercury and T = absolute temperature.

The dielectric constant of the oxychloride has been determined ³ at 0°, 10° and 20° C. by Schmidt's modification of Drude's method. By this method it has been shown that the liquid has a very high dielectric constant, 46.2 ± 1 at 20° C. and 51.00 ± 0.5 at 10° C., and solid selenium oxychloride has the constant 16.8 ± 2 at 0° C.

Sulphur, selenium and tellurium are soluble in the oxychloride in the cold, but on heating, reaction may take place. Sulphur interacts to form selenium monochloride, sulphur monochloride and sulphur dioxide. Tellurium is converted into its tetrachloride. Both red and yellow phosphorus react violently with the oxychloride, forming phosphorus pentoxide and selenium mono- and tetra-chlorides. Carbon, silicon and boron are unattacked.

Selenium oxychloride can be used to show that the essential differences between the adsorptive properties of "retorted" carbon and "activated" carbon are due to the presence of hydrocarbons in the former. After extraction of the hydrocarbons with selenium oxychloride the "retorted" carbon shows the same adsorptive properties as carbon which has been activated by steam at high temperatures.

The majority of the metals and their oxides interact with selenium oxychloride, the vigour of the reaction depending on the metal and on the temperature.⁴ Tungsten, tantalum and titanium are, however, only slightly attacked after long treatment at high temperatures, and the oxychloride may be employed as a reagent for the separation of molybdenum and tungsten or of niobium and tantalum.⁵ The behaviour of metallic sodium and potassium is interesting. The latter reacts explosively, whilst sodium is unaffected even when the oxychloride is

¹ Lenher, Smith and Town, *J. Physical Chem.*, 1922, 26, 156.

² Lenher, Smith and Town, *loc. cit.*

³ Wildish, *J. Amer. Chem. Soc.*, 1920, 42, 2607.

⁴ Ray, *ibid.*, 1923, 45, 2090.

⁵ See Merrill, *J. Amer. Chem. Soc.*, 1921, 43, 2383.

distilled over the metal. Copper reacts with the liquid in a sealed tube according to the equation

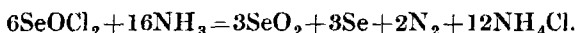


selenides being formed as intermediate products. Silver, nickel and cobalt react similarly, but very slowly; the reaction is more rapid with lead, but there is no evidence of intermediate selenide formation. With the oxides under similar conditions the metal chloride and selenium dioxide result; with red lead or lead dioxide, chlorine also is evolved.

Dry hydrogen sulphide interacts with selenium oxychloride with the formation of yellow selenium sulphide and evolution of hydrogen chloride. There is a development of heat which dissociates the selenium sulphide into sulphur and red selenium. Sulphur dioxide has no action on the hot anhydrous oxychloride, but if water is present there is a deposition of selenium. Sulphur trioxide is soluble in selenium oxychloride, forming a thick solution which is a very powerful solvent for the oxides of the rare earth metals. When the oxychloride is brought into contact with finely divided barium sulphate, the latter is at once peptised and becomes gelatinous in appearance,¹ but when subsequently treated with water the sulphate immediately changes back to the ordinary form.

When the oxychloride is warmed with potassium perdisulphate, chlorine is evolved; if sulphuric acid is present the reaction occurs in the cold. Chlorine is also evolved from selenium oxychloride when warmed with telluric or selenic acid.

Carbon monoxide has no action on selenium oxychloride.² Water causes decomposition of the liquid into selenium dioxide and hydrogen chloride. Anhydrous ammonia reacts according to the equation:



If the oxychloride is applied in dilute benzene solution some nitrogen selenide or selenium nitride is also formed.³ With liquid ammonia in the presence of ether in open vessels, the primary product is the compound $\text{SeOCl}_2 \cdot 4\text{NH}_3$, which is decomposed by water into selenium, selenium nitride, ammonium chloride, ammonium selenite and selenious acid; in a sealed tube, selenium nitride is formed in comparatively good yield.⁴

Protein materials such as hair and silk are soluble in the cold oxychloride, but cellulose is not affected.

Selenium oxychloride reacts with unsaturated hydrocarbons and ketones to form well-defined crystalline additive compounds,⁵ which, however, are not very stable, being readily decomposed by boiling water to yield their components.

It has been shown⁶ that when various rubbers are treated with the oxychloride, their physical properties are changed and they become amorphous powders, insoluble in the ordinary solvents for rubber. According to Frick the behaviour towards selenium oxychloride

¹ Lenher, *J. Amer. Chem. Soc.*, 1921, 43, 32.

² Lenher, *ibid.*, 1922, 44, 1664.

³ Lenher and Wolesensky, *ibid.*, 1907, 29, 215.

⁴ Strecker and Claus, *Ber.*, 1923, 56, [B], 362.

⁵ Müller, *Chem. Zeit.*, 1919, 43, 843.

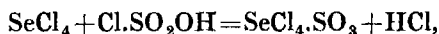
⁶ Frick, *J. Amer. Chem. Soc.*, 1923, 45, 1800.

indicates that there is no difference in empirical composition between the pure rubber hydrocarbon from the Hevea tree and the synthetic rubber made by polymerising isoprene with metallic sodium.

With some metallic chlorides, selenium oxychloride forms additive compounds, for example : ¹ $\text{TiCl}_4 \cdot 2\text{SeOCl}_2$, $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$, $\text{SbCl}_5 \cdot 2\text{SeOCl}_2$, $\text{FeCl}_3 \cdot 2\text{SeOCl}_2$, $\text{KCl} \cdot \text{SeOCl}_2$, $\text{RbCl} \cdot \text{SeOCl}_2$, $\text{CaCl}_2 \cdot 3\text{SeOCl}_2$, $\text{MgCl}_2 \cdot 3\text{SeOCl}_2$. The anhydrous chlorides of lithium, sodium, copper, silver, strontium, barium, zinc, cadmium, mercury, nickel and cobalt apparently do not combine with the oxychloride. Arsenic trichloride is miscible in all proportions.

When distilled with powdered sodium bromide, selenium oxychloride is converted into selenium oxybromide or selenyl bromide, SeOBr_2 , a dark red liquid which solidifies to yellow needles ² (see below).

Sulphur Selenium Oxytetrachloride, SeSO_3Cl_4 or $\text{SeCl}_4 \cdot \text{SO}_3$.—This can be produced by the direct combination of sulphur trioxide and selenium tetrachloride.³ It has also been obtained by heating selenium tetrachloride with chlorosulphonic acid, sulphuric acid, pyrosulphuric acid or sulphuryl chloride,



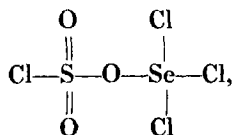
also by the action of pyrosulphuryl chloride on selenium (see p. 301),⁴ and by heating a mixture of sulphuryl and selenyl chlorides at 170° to 180°C . in a sealed tube :



The product of these reactions is a fairly stable colourless crystalline solid which melts at 165°C . and boils at 185°C . When vaporised it is largely dissociated, the vapour density at 210°C . being approximately one-third of the theoretical.

Water decomposes the substance with the formation of selenious, sulphuric and hydrochloric acids.

The constitution of the substance has been represented by the formula



but Prandtl and Borinski consider that it is better represented as a simple additive compound, $\text{SeCl}_4 \cdot \text{SO}_3$.

Selenium Oxybromide, SeOBr_2 , may be prepared ⁵ by adding the calculated amount of fused selenium to pure selenium dioxide in a cooled flask and dropping in the requisite quantity of bromine slowly. The mixture is then warmed until the whole of the oxide has dissolved.

The oxybromide is a reddish-yellow solid, melting at 41.5°C . It

¹ Wine, J. Amer. Chem. Soc., 1923, 45, 1235.

² Glauser, *Zeitsch. anorg. Chem.*, 1913, 80, 877.

³ Rose, *Ann. Phys. Chem.*, 1838, [ii.], 44, 315.

⁴ Claunziger, *Ber.*, 1878, 11, 2007; Prandtl and Borinski, *Zeitsch. anorg. Chem.*, 1909, 62, 237.

⁵ Leuther, J. Amer. Chem. Soc., 1922, 44, 1668.

has a boiling-point of 217°C . at 740 mm., with considerable decomposition. It decomposes so readily on heating that it cannot be purified by distillation even under reduced pressure. Its electrical conductivity is 6×10^{-5} mho at 40° to 50°C .

It is slowly converted by water into a mixture of selenious and hydrobromic acids. It is soluble in carbon disulphide, chloroform, benzene, toluene, xylene and carbon tetrachloride.

Selenium oxybromide is a very active chemical agent. It reacts with sulphur in the cold with the evolution of sulphur dioxide, and with selenium to form the monobromide. Phosphorus reacts violently with the solid; silicon and carbon are unattacked.

The majority of the metals react with selenium oxybromide with the production of the corresponding metal bromides, selenium dioxide and selenium monobromide. Zinc, cadmium, chromium, nickel, cobalt, tungsten and tantalum, however, are not attacked even after prolonged heating at 100°C .

Potassium chlorate liberates bromine from the oxybromide, whilst potassium perchlorate, permanganate, dichromate and chromium trioxide are without action on it.

By bubbling dry air at 60°C . through the oxybromide, bromine is liberated; this is stated by Lenher to be due to a primary dissociation into the dioxide and tetrabromide, followed by a secondary dissociation of the tetrabromide into the monobromide and bromine.

Carbon monoxide and sulphur dioxide have no action on the oxybromide.

Chloroselenic Acid, $(\text{SeO}_3 \cdot \text{HCl})_2$, has been described as a pale yellow liquid obtained when dry hydrogen chloride and selenium trioxide (see p. 331) are allowed to combine in a cooled vessel.¹ It has a density of 2.26, and solidifies at 46°C . It fumes in air owing to the escape of hydrogen chloride, which gas is also evolved on heating, selenium and selenium dioxide remaining.

Chloroselenic acid dissolves readily in water, much heat being evolved and selenic and hydrochloric acids being formed. It is decomposed by alcohol with precipitation of selenium. It dissolves without decomposition in selenium oxychloride, but is insoluble in benzene, carbon tetrachloride, chloroform and ether.

Molecular weight determinations give values in agreement with the double formula.

When *selenium dioxide* is similarly treated with dry hydrogen chloride, two *additive compounds*, $\text{SeO}_2 \cdot 4\text{HCl}$ and $\text{SeO}_2 \cdot 2\text{HCl}$, are obtained. The former is a yellow acicular crystalline solid, stable at 0°C ., whilst the latter is a yellow liquid stable up to 170°C . and distillable at this temperature with some decomposition into its constituents.² The liquid can absorb hydrogen chloride in amounts varying with the temperature. By the action of dehydrating agents selenium oxychloride may be obtained (see p. 321).

With hydrogen bromide, selenium dioxide produces a rather more stable crystalline compound, $\text{SeO}_2 \cdot 4\text{HBr}$.³

¹ Worsley and Baker, *Trans. Chem. Soc.*, 1923, 123, 2870.

² Ditte, *Ber.*, 1876, 9, 1130, 1432; *Ann. Chim. Phys.*, 1877, [v.], 10, 82; Parker and Robinson, *J. Chem. Soc.*, 1928, p. 2853; Hoffmann and Lenher, *J. Amer. Chem. Soc.*, 1929, 51, 3177.

³ Ditte, *loc. cit.*

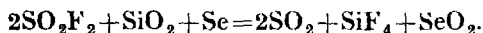
SELENIUM AND OXYGEN.

The affinity of selenium for oxygen is less than that of sulphur. The dioxide, SeO_2 , is well defined. The trioxide, SeO_3 , is much less stable than its sulphur analogue, and until recently all attempts to isolate it have been unsuccessful (see p. 331). Selenium sesquioxide, Se_2O_3 , has not been definitely isolated.¹ An oxide of composition Se_3O_4 has been described,² but its existence needs confirmation. The existence of a lower oxide, SeO , postulated to explain the characteristic odour of selenium when vaporised in air, is improbable.³

Selenium Dioxide, SeO_2 , may be prepared by the oxidation of selenium, either by burning in a stream of air or oxygen, or better by the use of a stream of nitrogen dioxide and oxygen, the latter process being capable of yielding a very pure product.⁴ If oxygen is passed in a rapid stream through fuming nitric acid and then over selenium heated to its melting-point, the selenium burns with a brilliant blue flame and a sublimate of dioxide is obtained.⁵ The more rapid the supply of oxygen the purer is the product. The dioxide thus obtained may be purified by sublimation in a current of pure dry oxygen. The oxidation appears to be greatly affected by catalytic influence, acidic substances acting as positive catalysts, while alkaline materials, including glass, act as negative catalysts. The dioxide is also precipitated when ozone is passed through a solution of selenium in selenium oxychloride.⁶

The oxidation can also be effected in the wet way by the use of nitric acid. The crude dioxide prepared in this way can be purified by sublimation.⁷

Sulphuryl fluoride in the absence of air reacts with selenium vapour in a glass vessel according to the equation: ⁸



Selenium dioxide forms lustrous, colourless, needle-shaped crystals, which readily sublime on warming. It has a density of 3.954 at 15° C.⁹ It can be fused by heating in a sealed tube to about 340° C.,¹⁰ the liquid being orange-yellow in colour, whilst the vapour is yellowish-green;¹¹ the change is reversible and the colour is not attributable to dissociation into selenium and oxygen. The crystals are hygroscopic and are soluble in water, alcohol, and sulphuric, selenic and acetic acids; one part of selenium dioxide dissolves in 2.67, 2.6 and 2.54 parts of water at 11.8°, 14° and 15.6° C., respectively. The solutions of the oxide in warm concentrated sulphuric and selenic acids are distinctly yellow, but become lighter in colour when cooled.

¹ Cameron and Macallan, *Proc. Roy. Soc.*, 1889, 46, 13.

² Konek, *Ber.*, 1918, 51, 872.

³ Sacc, *Ann. Chim. Phys.*, 1847, [iii.], 21, 119; Chabré, *ibid.*, 1890, [vi.], 20, 273; Peirce, *Amer. J. Sci.*, 1896, [iv.], 2, 163.

⁴ Meyer and Jannek, *Ber.*, 1913, 46, 2876.

⁵ Meyer, *ibid.*, 1922, 55, [B], 2082.

⁶ Hoffmann and Lenher, *J. Amer. Chem. Soc.*, 1929, 51, 3229.

⁷ Dennis and Koller, *ibid.*, 1919, 41, 949; also Thomsen, *Ber.*, 1869, 2, 598.

⁸ Moissan and Lebeau, *Bull. Soc. chim.*, 1902, [iii.], 27, 251.

⁹ Clausnizer, *Annalen*, 1879, 196, 265.

¹⁰ Chabré, *Ann. Chim. Phys.*, 1890, [vi.], 20, 202.

¹¹ Meyer and Langaer, *Ber.*, 1927, 60, [B], 285; Weller, *ibid.*, p. 649; Meyer, *ibid.*, p. 990.

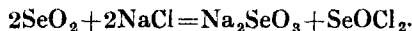
Selenium dioxide is an exothermic compound, the heat of formation being 57.2 Calories per gram-molecule, referred to vitreous selenium, whilst the value is somewhat less for the monoclinic element and less still for "metallic" selenium.¹

The absorption spectrum of selenium dioxide vapour contains groups of lines, particularly in the blue and violet.²

The dioxide is easily reducible to the element; when aqueous solutions are exposed to light, reddish-brown amorphous selenium slowly separates. The freezing-point, solubility and vapour pressure curves for the aqueous solutions indicate the presence of one hydrate only, namely the *monohydrate*, $\text{SeO}_2 \cdot \text{H}_2\text{O}$.³

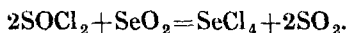
Heated in a current of hydrogen or in a sealed tube with sulphur (in the absence of air), the element is liberated, sulphur dioxide also being produced in the latter case.⁴ In the absence of moisture, sulphur dioxide does not reduce selenium dioxide,⁵ but hydroxylamine, hydrazine and phenylhydrazine reduce the solution in absolute alcohol.⁶

When heated with sodium chloride the dioxide gives a distillate of oxychloride : ⁷



Hydrogen chloride is absorbed with formation of unstable additive compounds, $\text{SeO}_2 \cdot 2\text{HCl}$ and $\text{SeO}_2 \cdot 4\text{HCl}$ (see p. 325), both of which dissociate readily. Additive compounds are also formed with hydrofluoric, hydrobromic and hydrocyanic acids.⁸

Sulphuryl chloride is without action on the dioxide, but thionyl chloride attacks it on warming, according to the equation : ⁹



Combination with sulphur trioxide readily occurs on warming, giving an easily fusible crystalline compound, $\text{SeO}_2 \cdot \text{SO}_3$, which does not fume in air; ¹⁰ the same product is obtainable by dissolving the dioxide in fuming sulphuric acid.¹¹ With ordinary hot sulphuric acid selenium is converted into the sulphoxide, SeSO_3 (see p. 338), hydrogen selenide and some amorphous selenium.¹²

Phosphorus pentachloride acts on selenium dioxide with the formation of the tetrachloride, whilst phosphorus trichloride yields brown amorphous selenium; in these reactions phosphorus oxychloride is also formed.

Carefully dried ammonia reacts with the dioxide in solution in absolute alcohol, the product having been variously described as *ammonium selenosamate*, $\text{NH}_2 \cdot \text{SeO}_2 \cdot \text{NH}_4$,¹³ and as an *ammonium ethyl-*

¹ Thomsen and Buike, *Thermochemistry* (Longmans, Green & Co., 1908), p. 245.

² Gernez, *Compt. rend.*, 1872, 74, 803.

³ Manchot and Ortner, *Zeitsch. anorg. Chem.*, 1922, 120, 300.

⁴ Klages, *Chem. Zeit.*, 1898, 22, 449; Krafft and Steiner, *Ber.*, 1901, 34, 560.

⁵ Schulze, *ibid.*, 1885, 18, 655.

⁶ Hinsberg, *ibid.*, 1891, 24, 5.

⁷ Cameron and Macallan, *Proc. Roy. Soc.*, 1890, 46, 35.

⁸ Prideaux and Millott, *J. Chem. Soc.*, 1926, p. 167; Ditte, *Ber.*, 1876, 9, 1130, 1432; *Ann. Chim. Phys.*, 1877, [v.], 10, 82.

⁹ Lenher and North, *J. Amer. Chem. Soc.*, 1907, 29, 33.

¹⁰ Metzner, *Ann. Chim. Phys.*, 1898, [vii.], 15, 231.

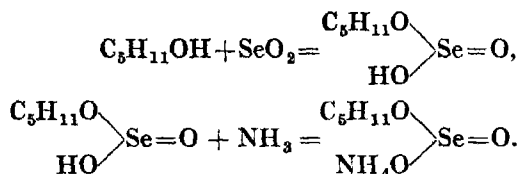
¹¹ Weber, *Ber.*, 1886, 19, 3185.

¹² de Coninck, *Compt. rend.*, 1906, 142, 571.

¹³ Cameron and Macallan, *Proc. Roy. Soc.*, 1888, 44, 112.

selenite, $C_2H_5O.SeO_2.NH_4$.¹ Possibly the nature of the product is dependent on the exact conditions prevailing during the reaction. Phosphine reacts in a different manner, the main products being free selenium and diethyl selenide.²

With a solution of selenium dioxide in *isoamyl* alcohol, ammonia throws down a white compound, which has been described as *ammonium amylselenite*, $NH_4.C_5H_{11}.SeO_3$. The reaction may be represented thus :



This ammonium amylselenite decomposes slowly on standing in air, liberating red selenium. The action of light hastens the rate of the decomposition.³ Hydrogen sulphide produces a dark orange-coloured precipitate from the solution in *isoamyl* alcohol.⁴

The oxidation potential of the system SeO_2-Se has been investigated.⁵

Selenious Acid, H_2SeO_3 .—If a concentrated solution of selenium dioxide in water is evaporated in a vacuum over sulphuric acid, crystals can be obtained having the composition H_2SeO_3 .⁶ Similar crystals can be obtained by recrystallising selenium dioxide from aqueous acetic acid, when the dioxide separates in the hydrated condition.⁷ Moist benzene may also be used as solvent.⁸

Selenious acid may be prepared directly from "anode slimes" by oxidising with nitric acid; on evaporating down to a syrupy consistency and allowing to cool, crystals of the crude acid may be obtained, which can be purified by repeated recrystallisation from water.⁹

Selenious acid is a crystalline solid having a density of 3.00 at 15° C.¹⁰ The crystals are deliquescent in moist air, whilst in dry air they gradually lose their combined water, with the formation of the dioxide; this loss of water is accelerated by heat. The acid is very soluble in water, solutions of it being obtained if selenium is oxidised in the presence of water.¹¹

Towards oxidising agents selenious acid is much more stable than sulphurous acid. This is in accordance with the observation that in a series of related elements, with increasing atomic weight there is generally a decrease in the relative stability of the higher oxidation products, as is illustrated by the groups N_2O_3 , N_2O_5 ; As_2O_3 , As_2O_5 ; Bi_2O_3 ,

¹ Divers and Haga, *Proc. Chem. Soc.*, 1899, 15, 101.

² Cameron, *Chem. News*, 1892, 66, 271.

³ Curtis and Burns, *J. Amer. Chem. Soc.*, 1917, 39, 37.

⁴ Curtis and Burns, *loc. cit.*

⁵ Carter, Butler and James, *J. Chem. Soc.*, 1926, p. 930.

⁶ Michaelis, *Zeitsch. Chem.*, 1870, [ii.], 6, 460.

⁷ Hinsberg, *Ber.*, 1891, 24, 5.

⁸ Chabré, *Ann. Chim. Phys.*, 1890, [vi.], 20, 202.

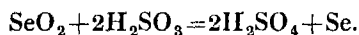
⁹ Dennis and Koller, *J. Amer. Chem. Soc.*, 1919, 41, 949.

¹⁰ Clausnizer, *Ber.*, 1878, 11, 2010.

¹¹ For density and freezing-point determinations on aqueous solutions of the acid, see de Coninck, *Bull. Acad. roy. Belg.*, 1905, p. 150; Rosenheim and Krause, *Zeitsch. anorg. Chem.*, 1921, 118, 177; Manchot and Ortnier, *ibid.*, 1922, 120, 302.

Bi_2O_3 ; and CO , CO_2 ; SnO , SnO_2 ; PbO , PbO_2 . The acid can be oxidised to selenic acid by strong oxidising agents¹ such as chlorine,² hypochlorites, potassium dichromate or permanganate. Nitric acid oxidises selenium only as far as selenious acid. There is no formation of intermediate compounds analogous to the dithionates in the oxidation of selenious acid (compare p. 125).

On reduction, selenious acid readily gives selenium; electrolysis of the aqueous solution therefore yields selenium at the cathode and selenic acid at the anode. With nascent hydrogen an aqueous solution of selenious acid will yield hydrogen selenide.³ Sulphurous acid, preferably in the presence of hydrochloric acid, also reduces selenious acid to selenium, which separates as a red precipitate:⁴



When this reduction is carried out in the presence of copper sulphate, as well as hydrochloric acid, the composition of the precipitate obtained varies from that of cuprous selenide in slightly acid solution, to pure selenium when the concentration of hydrochloric acid is high. It is probable that reduction to the element first occurs under all conditions, the subsequent formation of selenide depending on the hydrogen-ion concentration of the solution.⁵ Other reducing agents cause a similar separation of selenium, for example, hydriodic acid,⁶ phosphorous acid,⁷ hypophosphorous acid,⁸ hydroxylamine and hydrazine,⁹ and such organic substances as glucose, formic acid and formaldehyde.¹⁰ Sodium hydrosulphite also reduces a selenious acid solution,¹¹ and if used in the presence of a little sodium carbonate to remove any free acid, the formation of a red colloidal solution of selenium is so easily observed that a test will detect one part of selenious acid in 20,000 of water.¹²

Hydrogen sulphide reduces selenious acid solution with formation of a mixture of selenium and sulphur.¹³ The proportion of the two elements in the precipitate varies with the conditions. At one time this precipitate was regarded as a definite sulphide of selenium, but the sulphur can be entirely extracted by a mixture of benzene and carbon disulphide. The so-called "sulphur selenide" obtained by fusing together sulphur and selenium probably is also not a true compound, but only "mixed crystals" of the elements.¹⁴

The behaviour of manganese dioxide towards selenious acid solution

¹ Metzner, *Ann. Chim. Phys.*, 1898, [vn.], 15, 208, 230.

² For equilibrium measurements on the reactions with chlorine and bromine, see Sherrill and Izard, *J. Amer. Chem. Soc.*, 1928, 50, 1665.

³ Meunier, *Compt. rend.*, 1916, 163, 332.

⁴ Schulze, *Ber.*, 1885, 18, 655.

⁵ Clark, *J. Chem. Soc.*, 1928, p. 2388.

⁶ Perce, *Ber.*, 1896, 29, 1007; Gooch and Reynolds, *Amer. J. Sci.*, 1895, [in.], 50, 254. For equilibrium measurements on this reaction, see Schott, Swift and Yost, *J. Amer. Chem. Soc.*, 1928, 50, 721.

⁷ Gutbier, *Zeitsch. anorg. Chem.*, 1904, 41, 448.

⁸ Gutbier and Rohn, *ibid.*, 1903, 34, 448.

⁹ Jannasch and Müller, *Ber.*, 1898, 31, 2388.

¹⁰ de Coninck and Chauvenet, *Compt. rend.*, 1905, 141, 1234.

¹¹ Brunck, *Annalen*, 1904, 336, 281.

¹² Meyer and Jannck, *Zeitsch. anal. Chem.*, 1913, 52, 534; Meyer and von Garn, *ibid.*, 1914, 53, 29.

¹³ Rose, *Ann. Phys. Chem.*, 1837, [ii.], 42, 538.

¹⁴ Gutbier and Lohmann, *Zeitsch. anorg. Chem.*, 1904, 42, 325, 1905, 43, 384.

at 140° C. in a sealed tube is interesting. A yellow crystalline compound, MnSe_2O_8 , is obtained, not a selenium analogue of manganese dithionate, but a selenite of quadrivalent manganese. The substance is an oxidising agent, converting hydrochloric and arsenious acids into chlorine and arsenic acid, respectively.¹

Selenious acid forms a sparingly soluble crystalline additive compound with thiocyanic acid, known as "*thiocyanoselenious acid*," $\text{H}_2\text{SeO}_3 \cdot 2\text{HCNS}$. This is formed when a mixture of an alkali selenite and ammonium thiocyanate in aqueous solution is treated with fairly concentrated hydrochloric acid. When warmed with water it decomposes, liberating selenium.²

The Selenites.—Selenious acid is a weak acid but neutralises hydroxides and carbonates with the production of selenites. *Ammonium selenite* is formed by dissolving selenious acid in aqueous ammonia.³ The selenites can be obtained in an anhydrous condition by heating the metal oxides in a current of selenium dioxide vapour or with selenium dioxide in a sealed tube; in the latter case the products can be obtained crystalline if the selenium dioxide is used in excess.⁴

By treating a base with more than the equivalent amount of selenious acid, *acid selenites* may be obtained.⁵

The normal salts, on account of the feeble nature of selenious acid, are alkaline in solution. They exhibit a marked tendency to form complex salts; for example a series of *selenito salts* having bivalent central atoms with four co-ordination positions has been prepared⁶ by dissolving the normal selenites of cobalt, nickel, zinc, cadmium, manganese and copper in warm concentrated solutions of ammonium selenite and allowing to crystallise. *Molybdoselenites*⁷ and *vanadoselenites*⁸ have also been prepared,⁹ and a series of crystalline *uranyl salts* has been described.¹⁰ Alkali salts of the type $\text{MX} \cdot 2\text{SeO}_2 \cdot 2\text{H}_2\text{O}$ (where $\text{M} = \text{K}$ or NH_4 and $\text{X} = \text{Cl}$ or Br) are known,¹¹ and the potassium-chlorine salt when treated in solution with silver oxide yields silver chloride and a solution from which the *tetraselenite*, $\text{KHSeO}_3 \cdot \text{H}_2\text{SeO}_3$ or $\text{K}_2\text{O} \cdot 4\text{SeO}_2 \cdot 3\text{H}_2\text{O}$, may be crystallised. This substance at 100° C. loses only two-thirds of its water and may be considered as the *hydrogen pyroselenite*, $\text{KO} \cdot \text{SeO} \cdot \text{O} \cdot \text{SeO} \cdot \text{OH} + \text{H}_2\text{O}$, the chlorine compound from which it was derived then being the *chloropyroselenite*, $\text{KO} \cdot \text{SeO} \cdot \text{O} \cdot \text{SeO} \cdot \text{Cl}$.

Mercuric selenite, HgSeO_3 , prepared by the action of sodium hydrogen selenite on mercuric oxide, forms *double salts* of the types $\text{Na}_2\text{Hg}(\text{SeO}_3)_2$ and $\text{HgCl} \cdot \text{SeO}_3 \cdot \text{Na} \cdot 2\text{H}_2\text{O}$.¹²

The selenites are readily attacked by micro-organisms with the formation of a red substance, probably "metallic" selenium.¹³ The

¹ Marino and Squintani, *Atti R. Accad. Lincei*, 1911, [v.], 20, 1., 47.

² Ivanoff, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 661; *Chem. Zeit.*, 1908, 146, 931.

³ Cornec, *Ann. Chim. Phys.*, 1913, [viii.], 28, 697.

⁴ Espil, *Compt. rend.*, 1911, 152, 378.

⁵ Boulzourenano, *Ber.*, 1890, 23, 81.

⁶ Hahn, Meier and Sievert, *Zeitsch. anorg. Chem.*, 1926, 150, 126.

⁷ See this Series, Vol. VII., Part III., p. 161.

⁸ This Series, Vol. VI., Part III., p. 89.

⁹ Rosenheim and Krause, *Zeitsch. anorg. Chem.*, 1921, 118, 177.

¹⁰ This Series, Vol. VII., Part III., p. 322.

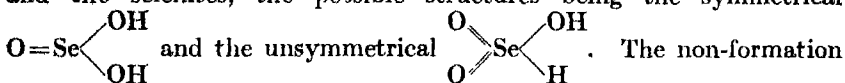
¹¹ Muthmann and Schäfer, *Ber.*, 1893, 26, 1008.

¹² Rosenheim and Pritze, *Zeitsch. anorg. Chem.*, 1909, 63, 275.

¹³ Gosio, *Atti R. Accad. Lincei*, 1904, [v.], 13, 1., 642.

alkali selenites act on the animal organism as irritant poisons.¹ Chabré has observed that the presence of 0.2 per cent. of selenious acid prevents the putrefaction of beef.

Constitution.—As with sulphurous acid and the sulphites, a decision is necessary between alternative formulæ for selenious acid and the selenites, the possible structures being the symmetrical



of a selenium analogue of thiosulphuric acid on heating selenium with a selenite solution may be regarded as slight evidence in favour of the symmetrical formula, which also receives a little support by the production of a symmetrical *ethyl selenite*, $\text{SeO}(\text{OC}_2\text{H}_5)_2$, by the action of ethyl iodide on silver selenite.²

Selenium Trioxide or Selenic Anhydride, SeO_3 .—All attempts to prepare this compound by methods analogous to those used for sulphur trioxide have failed, and it has been found impossible to isolate it by dehydration of selenic acid.

When a solution of selenium in selenium oxychloride is subjected for about 36 hours to a stream of ozonised oxygen, the red solution gradually becomes colourless and a white or very pale yellow precipitate appears which can be obtained free from oxychloride by washing first with carbon tetrachloride and then with ether. This solid was first obtained by Worsley and Baker,³ who concluded from analyses that it was selenium trioxide. It has a density of 3.6, is readily soluble in water with evolution of heat, forming selenic acid, and soluble also in alcohol. It is insoluble in benzene, carbon tetrachloride, chloroform and ether. On heating it decomposes at 120° C. without melting or subliming, yielding the dioxide. It combines with dry hydrogen chloride to form chloroselenic acid (see p. 325). The molecular weight, determined by cryoscopic methods using phosphorus oxychloride as solvent, corresponded with the formula SeO_3 .

A repetition of the foregoing work by Meyer and Pawletta,⁴ however, failed to confirm the production of selenium trioxide. According to these investigators, the dissolution of selenium in selenium oxychloride results in the formation of selenous chloride, and the precipitate obtained by the action of ozone is a mixture of this salt with selenium dioxide. Furthermore, substitution of carbon tetrachloride or glacial acetic acid for selenium oxychloride did not lead to the separation of the trioxide.

Selenic Acid, H_2SeO_4 .—This acid was first prepared by Mitscherlich in 1827, who suspended lead selenate in water and precipitated the lead by means of hydrogen sulphide. By the oxidation of aqueous solutions of selenious acid with suitable reagents, e.g. chlorine or bromine, selenic acid may also be obtained.⁵ When chlorine is used, any hydrogen chloride must be removed as soon as it is formed, for selenic acid is reduced by hot hydrogen chloride to selenious acid, with liberation of chlorine; the process is best carried out⁶ by passing a

¹ Chabré and Lapique, *Compt. rend.*, 1890, 110, 152.

² Michaelis and Landmann, *Ber.*, 1880, 13, 656; 1887, 20, 625.

³ Worsley and Baker, *Trans. Chem. Soc.*, 1923, 123, 2870.

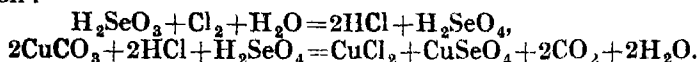
⁴ Meyer and Pawletta, *Ber.*, 1927, 60, [B], 985.

⁵ Thomsen, *ibid.*, 1869, 2, 598.

⁶ Meyer and Moldenhauer, *Zeitsch. anorg. Chem.*, 1921, 116, 193.

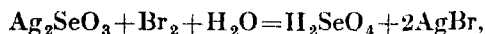
current of chlorine through a solution of selenious acid in nitric acid containing lead nitrate; by this means the hydrogen chloride produced is re-oxidised to chlorine, while the selenic acid separates as lead selenate.

By passing chlorine through a suspension of basic copper carbonate in aqueous selenious acid, copper selenate and copper chloride pass into solution:



On crystallisation, copper selenate separates, contaminated with about 1 per cent. of cupric chloride. The latter may be removed by extraction with acetone, in which it is readily soluble, whereas the selenate is only very slightly soluble; after this operation the copper selenate is finally purified by recrystallisation from water. The copper may then be removed by electrolysis,¹ using low current density, when selenic acid free from selenious acid and chlorine remains in the electrolyte. The solution may be concentrated until it contains about 82 per cent. of the acid by evaporating at 95° C. under reduced pressure.

Bromine oxidises silver selenite according to the equation



but the solution always contains a little selenious acid.²

A solution of selenious acid in nitric acid can be oxidised by electrolysis, when selenic acid is produced at the anode.³ This is one of the best methods for the preparation of selenic acid on the larger scale, for the product is generally free from all but a trace of selenious acid. The nitric acid solution can also be oxidised by heating with potassium bromate⁴ or permanganate.⁵

When selenious acid or a selenite is refluxed for about three hours with 30 per cent. hydrogen peroxide, oxidation proceeds to the extent of about 90 per cent.⁶

A convenient and efficient method for preparing selenic acid is based on the fact that under suitable conditions chloric acid completely oxidises selenium or selenious acid to the required acid. If selenium is used as the starting-point, it is oxidised to selenious acid using nitric acid as oxidising agent. The selenious acid is then oxidised by heating with barium chlorate and sulphuric acid; chlorine and oxides of chlorine are expelled in the process. By concentrating the liquid in a vacuum, any perchloric acid formed is removed, and the resulting solution may contain 85 to 90 per cent. of selenic acid.⁷

Pure selenic acid may be prepared from the solutions obtained in the foregoing processes by first neutralising with ammonia, precipitating barium selenate by the addition of barium chloride, and heating the separated precipitate with a solution containing the correct quantity of sulphuric acid. After removing the barium sulphate, a solution of pure selenic acid remains, and if this is concentrated as far as possible (see

¹ Dennis and Koller, *J. Amer. Chem. Soc.*, 1919, 41, 952.

² Dennis and Koller, *loc. cit.*

³ Meyer and Heider, *Ber.*, 1915, 48, 1154; Dennis and Koller, *loc. cit.*

⁴ Blumenthal, *Amer. J. Sci.*, 1913, [iv.], 35, 93.

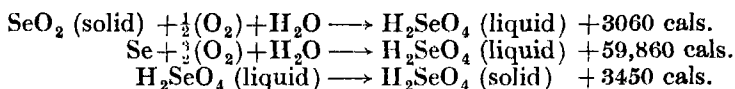
⁵ Mathers, *J. Amer. Chem. Soc.*, 1908, 30, 1374.

⁶ Huff and McCrosky, *ibid.*, 1929, 51, 1457.

⁷ Meyer and Moldenhauer, *Zeitsch. anorg. Chem.*, 1921, 116, 193.

p. 884) and then cooled to -50°C ., crystallisation sets in on stirring. The same result may be obtained by heating the concentrated solution in a vacuum at 180°C . and then cooling, a crystalline mass being formed.¹

Selenic acid crystallises in long hexagonal prisms, apparently isomorphous with crystalline sulphuric acid, and of melting-point 57° to 58°C . The density at 15°C . in the solid state is 2.951 and in the undercooled liquid condition 2.608. The molten substance is easily cooled below its melting-point without solidification, and the presence of small quantities of water lowers the melting-point to considerably under -50°C . On heating above 160°C . the acid is slowly decomposed with the formation of selenious acid and oxygen.² It can be distilled at 172°C . under a pressure of 85 mm.³ The following thermochemical data have been obtained :⁴



The vapour pressure of the liquid at different temperatures is as follows :⁵

$t, ^{\circ}\text{C}$.	100	105	140	190	210
p , mm. Hg.	15.8	21.0	28.3	32.0	37.0.

From the fact that in dilute solution the heats of neutralisation of selenic acid and sulphuric acid when neutralised by alkalis are approximately equal, it follows that these two acids are of comparable strength. Concentrated selenic acid resembles sulphuric acid in many of its properties, although its characteristics are rather less strongly marked. It absorbs moisture from the air, but on dilution with water it does not produce so much heat as sulphuric acid. As with sulphuric acid, determination of the freezing-point curve of mixtures with water indicates the existence of definite compounds or *hydrates*, viz., $\text{H}_2\text{SeO}_4 \cdot \text{H}_2\text{O}$ and $\text{H}_2\text{SeO}_4 \cdot 4\text{H}_2\text{O}$, the melting-points of which, $+26^{\circ}$ and -51.7°C . respectively, are given by the maxima on the freezing-point curve.⁶ The tetrahydrate appears to be isomorphous with the tetrahydrate of sulphuric acid, a crystal of the latter inducing crystallisation of the former.

Like sulphuric acid, selenic acid attacks many forms of organic matter, frequently with charring.⁷ Alcohol yields ethylene on heating, and cellulose (filter paper) is converted into a vegetable parchment. Toluene in the cold gradually undergoes concurrent oxidation and substitution with formation of *tolueneseleninic acid*, $\text{C}_6\text{H}_4\text{CH}_3 \cdot \text{SeO}_2\text{H}$, and *diphenylselenone dicarboxylic acid*.⁸

Selenic acid oxidises aniline with explosive violence.⁹

¹ Blumenthal, *Amer. J. Sci.*, 1913, [iv.], 35, 93.

² Meyer and Moldenhauer, *loc. cit.*

³ Stöcker and Krafft, *Ber.*, 1906, 39, 2198.

⁴ Metzner, *Compt. rend.*, 1898, 127, 52.

⁵ Metzner, *loc. cit.*

⁶ Kremann and Hofmeier, *Monatsh.*, 1908, 29, 1111.

⁷ de Coninck and Chauvenet, *Ann. Chim. anal.*, 1916, 21, 114.

⁸ Doughty and Elder, *Eighth Intern. Congr. Appl. Chem.*, 1912, 6, 93.

⁹ Meyer and Wagner, *Ber.*, 1922, 55, [B], 1216.

SULPHUR, SELENIUM, AND TELLURIUM.

Sulphur is soluble in liquid selenic acid, forming a deep blue solution; on warming this solution to about 65° C. the selenic acid undergoes marked reduction, with formation of selenious acid and selenium. This result serves to emphasise the already observed lower stability of the oxygen compounds of selenium, and therefore their higher oxidising power, compared with the corresponding sulphur compounds.¹ It has been suggested that the blue colour of a sulphur solution in selenic acid and the green colour of a selenium solution in sulphuric acid are due to the production of isomeric substances SSeO_3 and SeSO_3 , sulphur selenoxide and selenium sulphoxide, respectively; the assumption of such isomerism is made on very slight evidence. For a fuller account of selenium sulphoxide, see p. 338.

Selenium likewise dissolves in selenic acid, giving a deep green solution, the colour of which has been attributed to the formation of an unstable oxide, selenium sesquioxide, Se_2O_3 (analogous to S_2O_3), which, however, has not yet been isolated. The colour disappears on warming, with formation of selenious acid, but if the cold coloured solution is diluted, the selenium separates out. Tellurium gives a purple-red solution; if this colour is due to a compound TeSeO_3 , analogous to the foregoing sesquioxide, the compound must be exceedingly unstable, as slight warming destroys the colour.²

It might be expected by analogy with sulphuric acid that selenic acid would absorb nitrogen dioxide with the formation of a nitrosylselenic acid, $\text{NO}_2\cdot\text{SeO}_3\text{H}$, but this is not the case. Nitrogen dioxide is absorbed, however, at low temperatures, the product being an unstable blue solid, probably $\text{SeO}_2(\text{NO}_2)_2$, which melts with decomposition at -13°C .³ (cf. p. 341). Nitrosylselenic acid may be obtained by the action of excess of liquid nitrogen trioxide on anhydrous selenic acid which is kept ice-cold. The product is a white crystalline "snow-like" mass, having a melting-point of 80°C ., with decomposition. It is unstable even at ordinary atmospheric temperatures and is immediately decomposed by water.⁴

Aqueous solutions⁵ of selenic acid cannot, by distillation under ordinary pressure, be entirely deprived of their water without decomposition. Until a temperature of 205°C . is reached the distillate consists almost entirely of water, the residual liquid being about 88 per cent. selenic acid. Above this temperature the selenic acid is slightly volatile and a distillate of very dilute selenic acid is obtained, the residual liquid finally attaining a composition of approximately 96 per cent. and a temperature of nearly 290°C . Then decomposition begins to occur with formation of selenium dioxide, oxygen and water. By distilling under reduced pressure, the high temperature is avoided, and a residue of selenic acid of almost 100 per cent. concentration is obtained at a temperature near 180°C .⁶

¹ Kraft and Steiner, *Ber.*, 1901, 34, 560; Benger, *J. Amer. Chem. Soc.*, 1917, 39, 2171.

² Cameron and Macallan, *Proc. Roy. Soc.*, 1890, 46, 30.

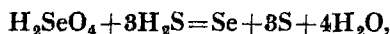
³ Lenher and Matthews, *J. Amer. Chem. Soc.*, 1906, 28, 516.

⁴ Meyer and Wagner, *Ber.*, 1922, 55, [B], 690.

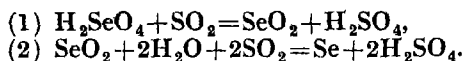
⁵ For the specific gravity of aqueous selenic acid at various concentrations, see Cameron and Macallan, *Proc. Roy. Soc.*, 1890, 46, 30; for the electrical conductivity, see Ostwald, *J. prakt. Chem.*, 1885, [ii.], 32, 313; Miolati, *Gazzetta*, 1901, 31, i., 105; for the molecular refraction, see Gladstone and Hibbert, *Trans. Chem. Soc.*, 1895, 67, 846.

⁶ Pettersson, *Zeitsch. anorg. Chem.*, 1873, 12, 287; Gooch and others, *Amer. J. Sci.*, 1895, [iii.], 50, 254, 400, 402.

Aqueous solutions of selenic acid will, on heating, oxidise hydrochloric, hydrobromic and hydriodic acids. Hydrogen sulphide gas at any temperature above -10° C. causes decomposition of selenic acid, the rate of reaction increasing both with the temperature and the concentration of the acid. The complete reaction may be represented by the equation



but the mechanism of the reaction is more complicated.¹ Solutions of selenic acid of all concentrations are reduced by selenium, especially on warming; with sulphur the reaction takes place more slowly and higher temperatures are necessary. The reaction with sulphur dioxide takes place in two stages and selenium dioxide may be separated as an intermediate product:



When the sulphuric acid reaches a certain concentration, the reducing action stops, but when the solution is diluted the reaction can proceed to completion.²

By the action of hydrazine hydrate on a dilute solution of selenic acid, hydrazine hydrogen selenate may be obtained as a colourless compound which is not decomposed by boiling water, but which, when dry, explodes with great readiness when subjected to heat, to shock, or to fumes of hydrogen chloride. For this reason, before hydrazine hydrate is used in the analysis of selenium compounds (see p. 307), it is essential that selenic acid and selenates should be reduced to selenites by means of hydrochloric acid.³

When selenic acid and molybdic acid are heated together on a water-bath for several days a compound of composition $\text{MoO}_3 \cdot \text{SeO}_3$ is formed, which is obtainable as a crystalline mass,⁴ and which with a little water yields a hydrate, having the formula $\text{MoO}_3 \cdot \text{SeO}_3 \cdot 2\text{H}_2\text{O}$ when dried at 110° C. This compound has the properties of a tetrabasic acid.

Aqueous selenic acid is a solvent for metals, such as magnesium and zinc, hydrogen being evolved. With metallic iron there is only slight action (contrast sulphuric acid); after some time a thin deposit of red selenium forms on the iron, due to reduction of the acid by the nascent hydrogen produced.⁵ Copper and gold are dissolved by the warm acid, selenious acid being formed simultaneously; the power of dissolving gold must be ascribed as much to the oxidising power of the acid as to its acidity.⁶ There is no appreciable action with osmium in the cold, but at about 120° C. a colourless solution is obtained containing osmium tetroxide; no selenate is formed, the other product of the reaction being selenious acid.⁷

The Selenates.⁸—Selenic acid resembles sulphuric acid in being dibasic and both normal and acid salts are known. The salts can be

¹ Benger, *J. Amer. Chem. Soc.*, 1917, 39, 2171; cf. Gooch and Blumenthal, *Amer. J. Sci.*, 1913, [iv.], 35, 54.

² Meyer and Aulich, *Ber.*, 1928, 61, [B], 1839.

³ See Wendehorst, *Zeitsch. anorg. Chem.*, 1928, 176, 233.

⁴ Tutton, *Chem. News*, 1918, 170, 30.

⁵ Cameron and Davy, *ibid.*, 1881, 44, 63; Warren, *ibid.*, 1890, 61, 100.

⁶ Hradecky, *Oesterr. Chem. Zeit.*, 1917, [2], 20, 43.

⁷ Details of the preparation and properties of the various metal selenates are given under the individual metals in other volumes of this Series.

⁸ Benger, *loc. cit.*

obtained from the acid by the generally recognised methods, or the corresponding selenites may be oxidised, e.g. by fusion with sodium peroxide¹ or by electrolysis in aqueous solution using platinum foil as anode and platinum wire as cathode. Very little selenium is formed at the cathode and most of the solute is converted into selenate at the anode.²

The normal *selenates* of *potassium, sodium, calcium and magnesium* are very similar in properties to the corresponding sulphates, except that the potassium salt is much more soluble in water than potassium sulphate.³ Sodium selenate gives a decahydrate which effloresces, and the transition-point between this and the anhydrous salt is 31.8° C., above which point the solubility falls as the temperature rises. Calcium selenate gives a hemihydrate resembling plaster of Paris, and also a hydrate of composition $\text{CaSeO}_4 \cdot 1.5\text{H}_2\text{O}$.⁴

The selenates give many other examples of isomorphism with the sulphates, and therefore also with the chromates and manganates, and mixed crystals are easily obtained.⁵ The selenates, however, frequently take and retain their water of crystallisation less readily than the corresponding sulphates.

With the exception of the calcium, strontium, barium and mercurous salts, the normal selenates are readily soluble in water. Barium chloride and mercurous nitrate are therefore convenient precipitation agents.⁶ *Barium selenate* is, however, more soluble than barium sulphate, and also differs from the latter salt in being slowly reduced to selenite by hydrochloric acid;⁷ for these reasons precipitation with barium chloride is not applicable to the quantitative determination of selenic acid. A concentrated solution of selenic acid which has been saturated with barium selenate deposits crystals of *barium selenic acid*, $\text{H}_2[\text{Ba}(\text{SeO}_4)_2]$.⁸

Copper selenate, like the corresponding sulphate, is best known in the form of the pentahydrate. When the latter is dehydrated at 102° C. it is converted into the monohydrate, dehydration being complete at 230° to 235° C. Copper selenate can also be obtained in the trihydrated form.⁹

By the action of ammonia on copper selenate pentahydrate, small bluish-violet needle-like crystals of *copper selenate tetrammoniate monohydrate*, $\text{CuSeO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$, are obtained. On exposure to the air these crystals slowly evolve ammonia and become dull in appearance. They are soluble in water, giving a deep blue solution, which on dilution becomes lighter in colour and deposits basic copper salts. When the crystals are exposed to the action of air for many hours, the preliminary evolution of ammonia ceases and the blue product has the composition $\text{CuSeO}_4 \cdot 3\text{NH}_3 \cdot \text{H}_2\text{O}$. When the bluish-violet crystals of the tetrammoniate monohydrate are dried over lime in a desiccator under a low

¹ Meyer and Heider, *Ber.*, 1915, 48, 1154. See also Mathers and Graham, *J. Amer. Chem. Soc.*, 1929, 51, 3229.

² Müller, *Ber.*, 1903, 36, 4262.

³ Etard, *Ann. Chim. Phys.*, 1894, 2, 503; Tutton, *Trans. Chem. Soc.*, 1897, 71, 846; Friend, *ibid.*, 1929, p. 2782.

⁴ Meyer and Aulich, *Zeitsch. anorg. Chem.*, 1928, 172, 321.

⁵ Michel, *Compt. rend.*, 1888, 106, 878; Pettersson, *Ber.*, 1876, 9, 1676; Tutton, *Zeitsch. Krist. Min.*, 1897, 29, 63.

⁶ Denigès, *Ann. Chim. anal.*, 1915, 20, 57.

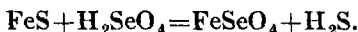
⁷ Rose, *Ann. Phys. Chem.*, 1855, [ii.], 95, 426.

⁸ Meyer and Friedrich, *Zeitsch. physikal. Chem.*, 1922, 101, 498.

⁹ Dennis and Koller, *J. Amer. Chem. Soc.*, 1919, 41, 964.

pressure for some days, they lose their water but not their ammonia, and light blue-violet crystals of $\text{CuSeO}_4 \cdot 4\text{NH}_3$ are obtained. On exposure to the air these crystals evolve ammonia, but kept over lime they are quite stable.¹

Ferrous selenate can be prepared by the action of selenic acid on ferrous sulphide; selenic acid does not dissolve iron (see p. 335):



The production of the hydrogen sulphide serves to prevent the selenate being oxidised to the ferric state. There may also be a slight secondary reaction resulting in the precipitation of both sulphur and selenium according to the equation on p. 335. From the solution unstable monoclinic crystals of hydrated ferrous selenate, $\text{FeSeO}_4 \cdot 7\text{H}_2\text{O}$, may be deposited.

The stability of the product is greatly increased by mixing the solution with the equivalent amount of one of the alkali selenates, when crystals of a double selenate, of the type $\text{M}_2\text{SeO}_4 \cdot \text{FeSeO}_4 \cdot 6\text{H}_2\text{O}$,² are deposited.

In the ready formation of *double salts*, selenates show further resemblance to the sulphates, and even "*alums*," e.g. $\text{M}_2\text{SeO}_4 \cdot \text{Al}_2(\text{SeO}_4)_3 \cdot 24\text{H}_2\text{O}$, $\text{M}_2\text{SeO}_4 \cdot \text{Cr}_2(\text{SeO}_4)_3 \cdot 24\text{H}_2\text{O}$ and $\text{M}_2\text{SeO}_4 \cdot \text{Fe}_2(\text{SeO}_4)_3 \cdot 24\text{H}_2\text{O}$ (where M represents one of the alkali metals), have been prepared and found to be of the orthodox crystalline form.³ Monoclinic double selenates of the copper, iron and cobalt groups with the alkali metals have also been prepared,⁴ as well as the following:⁵ $\text{K}_2\text{SeO}_4 \cdot \text{MgSeO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{SeO}_4 \cdot \text{MgSeO}_4 \cdot 4\text{H}_2\text{O}$, $\text{K}_2\text{SeO}_4 \cdot \text{CaSeO}_4 \cdot 2\text{H}_2\text{O}$. The last is interesting in that the corresponding sulphate is a monohydrate. No double selenate corresponding with glaserite, $2\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$, has been obtained.

The selenates are not so harmful as the selenites in their physiological action, and it is probable that what poisonous nature they possess is dependent on their previous reduction in the organism to selenite.⁶

Perselenic Acid.—Electrolysis of a cold concentrated solution of potassium selenate containing some free selenic acid has been found to produce a similar effect to that observed with the corresponding sulphate.⁷ A potassium perselenate was formed at the anode, the chemical process probably being of the same nature as in the formation of perdisulphate, but on account of its instability the product was not obtainable in a higher degree of purity than approximately 75 per cent.

According to Worsley and Baker⁸ the compounds described by them as selenium trioxide and chloroselenic acid (*q.v.*) both react with hydrogen peroxide to produce a perselenic acid.

¹ Dennis and Koller, *loc. cit.*

² Tutton, *Chem. News*, 1918, 170, 30.

³ von Gerichten, *Annalen*, 1873, 168, 214; Fabre, *Compt. rend.*, 1887, 20, 543; Pettersson, *Ber.*, 1873, 6, 1466.

⁴ See Tutton, *Proc. Roy. Soc.*, 1918, [A], 94, 352; 1919, [A], 96, 156; 1920, [A], 98, 67; *Phil. Trans.*, 1919, [A], 218, 395.

⁵ Meyer and Aulich, *loc. cit.*

⁶ Jones, *Biochem. J.*, 1909, 4, 405; 1911, 6, 106.

⁷ Dennis and Brown, *J. Amer. Chem. Soc.*, 1901, 23, 258.

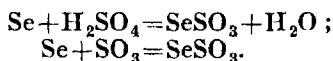
⁸ Worsley and Baker, *Trans. Chem. Soc.*, 1923, 123, 2870.

COMPOUNDS CONTAINING SELENIUM AND SULPHUR.

As already mentioned (p. 329), it is probable that all attempts to prepare a compound of sulphur and selenium, either by heating the elements together or by reducing selenious acid with hydrogen sulphide, give rise only to a conglomerate of sulphur and selenium, or at the best to mixed crystals containing these elements; that is to say, solid solutions of the one element in the other are obtained.¹ Such a mixture may be obtained as a yellow precipitate by saturating a solution of aluminium chloride (containing 100 mgms. Al per litre) with hydrogen sulphide and at the same time running in selenious acid. If the dried precipitate is applied in a thin layer to smooth, dense, but not highly glazed, paper, a sensitive reagent for mercury vapour is obtained.² The paper is darkened by the vapour, the shade varying with the concentration of the vapour, the time of exposure and the temperature; for example, in a test with air containing one part of mercury in four millions, on passing the sample over the paper at a velocity of 1 metre per sec. and at 70° C. a colour change was observed after four minutes. The paper is not affected by solutions containing mercury ions.

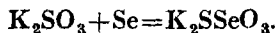
There are, however, compounds containing sulphur and selenium, with one or more additional elements, in which the selenium may be regarded as having partially displaced sulphur from a compound containing more than one atomic proportion of this element.

Selenium Sulphoxide or Sulphur - Selenium Sesquioxide, SeSO_3 .—This has already been mentioned in connection with the solubility of selenium in sulphuric acid (pp. 291, 300) as the probable cause of the green colour produced. It is also obtainable, similarly to sulphur sesquioxide, from fluid sulphur trioxide by the addition of powdered amorphous selenium, the sulphoxide being insoluble in the sulphur trioxide, so that the latter can be decanted off:



It is described as a green liquid, solidifying to a green solid, which easily passes into a yellow modification. It is slightly more stable than sulphur sesquioxide, but decomposes on gentle heating.³ The compound $\text{SeO}_2 \cdot \text{SO}_3$ has already been mentioned (p. 327).

Selenosulphuric Acid or Thioselenic Acid, H_2SSeO_3 .—Salts of this acid are obtained when finely divided selenium is dissolved by warming with an aqueous solution of an alkali sulphite, potassium sulphite being the most satisfactory:⁴



The *selenosulphates* are very unstable and their solutions undergo partial decomposition with separation of red selenium even on mere

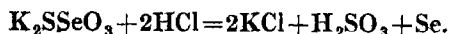
¹ Gutbier and Lohmann, *Zeitsch. anorg. Chem.*, 1904, 42, 325; 1905, 43, 384; Muthmann, *Zeitsch. Kryst. Min.*, 1890, 17, 357; Bettendorff and von Rath, *Ann. Phys. Chem.*, 1870, [ii.], 139, 329; Ringer, *Zeitsch. anorg. Chem.*, 1902, 32, 183.

² Nordlander, *Ind. Eng. Chem.*, 1927, 19, 518, 522.

³ Weber, *Ann. Phys. Chem.*, 1875, [ii.], 156, 547; Divers and Shimose, *Trans. Chem. Soc.*, 1884, 45, 194; 1886, 49, 583; de Coninck, *Compt. rend.*, 1906, 143, 682; Moles, *Anal. Fis. Quim.*, 1916, 13, 134.

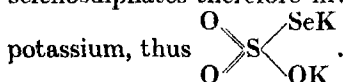
⁴ Cloéz, *Bull. Soc. chim.*, 1861, 11, 112; Rathke, *J. prakt. Chem.*, 1864, 92, 141; 1865, 95, 1.

dilution with water. The addition of acids immediately effects decomposition with formation of selenium, selenosulphuric acid itself being incapable of free existence :



The addition of iodine also brings about immediate decomposition with liberation of selenium.

The evidence supplied by the method of formation and the occurrence of isomerism as to analogous structures for the thiosulphates and selenosulphates, is amplified by the chemical behaviour of the potassium alkyl selenosulphates, obtained by treatment of potassium selenosulphates with alkyl halides.¹ These, on electrolytic reduction and also on oxidation with hydrogen peroxide, yield the corresponding diselenides (compare the thiosulphates, p. 203). The structure of the selenosulphates therefore involves a selenium atom directly attached to



Selenotrithionic Acid, $\text{H}_2\text{SeS}_2\text{O}_6$.—In the preparation of potassium selenosulphate as just described, a certain small amount of a potassium selenotrithionate, $\text{K}_2\text{SeS}_2\text{O}_6$, is obtained, which generally crystallises first on evaporation of the solution at the ordinary temperature. The yield is much better if potassium hydrogen sulphite is also present with the selenium and normal potassium sulphite.²

The corresponding free acid is formed by the interaction of aqueous solutions of sulphurous and selenious acids, the former in excess :



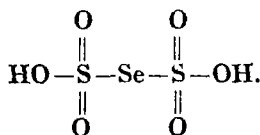
In the description of the properties of selenious acid it was mentioned that the acid is reduced by sulphurous acid in the presence of hydrochloric acid. In the absence of hydrochloric acid the separation of selenium may be far from complete or even entirely lacking, on account of the formation of selenotrithionic acid.³

Selenotrithionic acid is known only in aqueous solution and in the form of its salts. The solution is not very stable and on exposure to light gradually deposits selenium. Evaporation also causes decomposition. Hydrochloric acid in considerable quantity causes decomposition (compare above) with liberation of selenium :



The *selenotrithionates* are rather more stable than the acid, but they yield a precipitate of selenium when warmed with hydrochloric acid. As the barium salt is soluble in water, no precipitate is produced on the addition of barium chloride.

From the general behaviour of the acid and its salts the constitution is presumably



¹ Price and Jones, *Trans. Chem. Soc.*, 1909, 95, 1729; Twiss, *ibid.*, 1914, 105, 36, 1672.

² Rathke, *J. prakt. Chem.*, 1865, 95, 8; 1866, 97, 56.

³ Schulze, *Ber.*, 1885, 18, 656.

Diselenotritithionic Acid, $\text{H}_2\text{Se}_2\text{SO}_6$.—If in the interaction of selenious and sulphurous acids an excess (that is, more than a semi-molecular proportion) of the former is taken, the odour of sulphur dioxide soon disappears and apparently a diselenotritithionic acid is formed in the solution :¹



The acid is even less stable than selenotritithionic acid ; its aqueous solution decomposes in the light or on warming ; in fact, it cannot even be preserved in the dark. Acids and alkalis also bring about its decomposition. Treatment with barium carbonate, as in the case of the preceding acid, gives a solution of the barium salt which, however, is less stable than barium selenotritithionate, and the solution decomposes slowly in the dark.

Selenopentathionic Acid, $\text{H}_2\text{SeS}_4\text{O}_6$, is stated to be formed as the sodium salt when sodium thiosulphate and selenious acid interact in the presence of dilute hydrochloric acid. The reaction is described as taking place according to the equation



but the result cannot be considered as absolutely proved, for the salt cannot be isolated, being decomposed when the solution is concentrated either by warming or in a vacuum.²

SELENIUM AND NITROGEN.

Selenium Nitride, Se_4N_4 .—This was first obtained in 1859 by saturating selenium tetrachloride with ammonia in the cold :³



It may also be prepared by passing a stream of dry ammonia into a 2 to 4 per cent. solution of selenyl chloride in benzene.⁴ The nitride is precipitated as a buff-coloured solid which becomes orange-red when dry. Some free selenium is deposited along with the nitride, the amount increasing with the concentration of the selenyl chloride solution. After washing the buff precipitate the free selenium may be extracted by means of potassium cyanide solution.

By each of these methods the nitride is obtained as a brick-red amorphous powder which, when dry, is highly explosive, detonating violently on slight touch, forming a cloud of red selenium ; it is considerably more sensitive than mercury fulminate.

After investigating the action of liquid ammonia on a variety of selenium compounds, Strecker and Claus⁵ have come to the conclusion that the tetrahalides are the best initial materials for the preparation of selenium nitride. The action of liquid ammonia on selenium tetrabromide in the presence of carbon disulphide gives a good yield of the nitride.

Selenium nitride is insoluble in water, alcohol and ether, slightly

¹ Schulze, *J. prakt. Chem.*, 1885, [2], 32, 390.

² Norris and Fay, *Amer. Chem. J.*, 1900, 23, 119.

³ Espenschied, *Annalen*, 1860, 113, 101.

⁴ Lenher and Wolesensky, *J. Amer. Chem. Soc.*, 1907, 29, 21.

⁵ Strecker and Claus, *Ber.*, 1923, 56, [B], 362.

soluble in carbon disulphide, benzene and glacial acetic acid. It is decomposed by caustic potash with the formation of potassium selenite, ammonia and free selenium. It reacts explosively with both chlorine and bromine. In the presence of carbon disulphide the action of bromine leads to the formation of a brownish-green hygroscopic substance having the composition SeN_2Br_4 .¹ If the bromine vapour is diluted with carbon dioxide, the nitride is converted into *ammonium selenibromide*, $(\text{NH}_4)_2\text{SeBr}_6$, the formation of which appears to be due to the action of atmospheric moisture on a primary addition product. In similar circumstances chlorine yields a compound of composition SeNCl_3 . Iodine, whether solid or dissolved in ether or chloroform, has no action on selenium nitride.¹

A suitable solvent is not available for the determination of the molecular weight of the nitride, but evidence seems to favour a cyclic structure for the molecule Se_4N_4 .¹

Nitrosylselenic Acid, $\text{NO.O.SeO}_2\text{OH}$.—An attempt to prepare this compound by the action of liquid nitrogen tetroxide on concentrated selenic acid, cooled with solid carbon dioxide, resulted in the formation of a dark blue solid, the composition of which suggested it to be the compound $\text{SeO}_2(\text{O.NO})_2$.² It melted at -13°C . and above this temperature decomposed into its components. The blue colour may, however, be attributed to the decomposition of the nitrogen tetroxide by the action of water to form nitrogen trioxide and nitric acid,³ for when the reagents are mixed there is a separation into two layers, the upper containing nitrogen trioxide, nitric acid and a little selenic acid, whilst the lower is a mixture of nitrogen trioxide and selenic acid. The lower layer solidifies when sufficiently cooled, and on gently warming then decomposes into nitric oxide and nitrosylselenic acid, which is colourless.

The acid is best prepared by the action of a large excess of liquid nitrogen trioxide on ice-cold anhydrous selenic acid.⁴ The excess of liquid trioxide is subsequently allowed to evaporate away.

Nitrosylselenic acid is a colourless crystalline snow-like mass, which melts at 80°C . with decomposition. It is unstable even at atmospheric temperatures and is immediately decomposed by water.

A *blue compound*, apparently analogous to sulphonitronic acid (p. 251), is formed on the addition of mercury to a solution of nitrosylselenic acid in selenic acid monohydrate,⁵ or by reducing a solution of sodium nitrite in concentrated selenic acid by means of mercury. The presence of copper selenate facilitates the reaction. The selenonitronic acid is very readily oxidised and appears to be stable only in the presence of concentrated selenic acid.

SELENIUM AND PHOSPHORUS.

Five selenides of phosphorus are known, viz. P_4Se , P_2Se , P_4Se_3 , P_2Se_3 and P_2Se_5 .

Phosphorus Subselenide, P_4Se , may be prepared by heating one

¹ Strecker and Claus, *loc. cit.*

² Lenher and Matthews, *J. Amer. Chem. Soc.*, 1906, 28, 516.

³ Meyer and Gulbins, *Ber.*, 1926, 59, [B], 456.

⁴ Meyer and Wagner, *ibid.*, 1922, 55, [B], 690.

⁵ Meyer and Gulbins, *loc. cit.*

atomic proportion of selenium with at least four atomic proportions of phosphorus in the presence of an inert gas. The product obtained may contain a little red phosphorus which can be got rid of by filtration. Phosphorus subselenide is a yellow oily liquid which crystallises at -12° C. and is soluble in carbon disulphide. It is spontaneously inflammable in air and is decomposed by alkalis on heating, with liberation of phosphine.

Phosphorus Monoselenide, P_2Se , may be obtained by heating one atomic proportion of selenium with two atomic proportions of phosphorus in a current of hydrogen. It is formed with incandescence as a clear red solid, which is combustible and slightly soluble in carbon disulphide. It is decomposed by boiling alkalis with liberation of phosphine. With metal selenides it forms double selenides.

Tetraphosphorus Triselenide, P_4Se_3 , is readily prepared¹ by the action of yellow phosphorus on powdered selenium in boiling tetrahydronaphthalene. The crude substance crystallises from the solution and may be purified by extraction with a mixture of light petroleum and carbon disulphide. The colour of the selenide varies from yellow to orange-red, according to the thickness of the layer under observation. The density at 22° C. is 3.161. On being heated the selenide exhibits distinct phosphorescence above 160° C. and melts at about 242° C.; at 280° C. the phosphorescence is very marked. The compound is slowly decomposed by moisture, and reacts with alkali hydroxides, sulphides and carbonates to form alkali selenide.

Phosphorus Triselenide or Phosphorous Selenide, P_2Se_3 .—This compound may be obtained by heating together phosphorus and selenium in the requisite atomic proportions. The reaction is accompanied by a great evolution of heat. The product is a ruby-red solid, which is combustible on heating. It is insoluble in carbon disulphide. With metal selenides it forms double selenides of the type $P_2Se_3 \cdot 2MSe$.²

Phosphorus Pentaselenide or Phosphoric Selenide, P_2Se_5 , may be prepared³ by melting together phosphorus and selenium in the atomic proportions until combination takes place.

It is a reddish-brown solid, insoluble in carbon disulphide. It dissolves in carbon tetrachloride on heating, from which solution it crystallises out in black needles on cooling.⁴ It is decomposed by heat and burns, leaving a residue of selenium. It combines with the selenides of certain metals, e.g. copper and silver, forming double selenides.⁵

Attempts to prepare phosphorus thioselenides from the components in tetrahydronaphthalene, in a manner similar to that used for tetraphosphorus triselenide, have failed to produce any definite compounds.⁶

Phosphorus Chloroselenide, $PSeCl_2$.—By treating phosphorus pentachloride with selenium tetrachloride, phosphorus chloroselenide has been obtained as a yellow substance which becomes red on heating.⁷

Selenophosphates and Oxyselenophosphates.—By the action of phosphorus pentaselenide on aqueous solutions of the selenides of

¹ Mai, *Ber.*, 1926, 59, [B], 1888; 1928, 61, [B], 1807.

² Hahn, *J. prakt. Chem.*, 1864, 93, 430.

³ Rathke, *Annalen*, 1869, 152, 181.

⁴ Hahn, *loc. cit.*

⁵ Baudrimont, *Ann. Chim. Phys.*, 1864, [4], 2, 5.

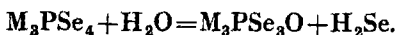
⁶ Hahn, *loc. cit.*

⁷ Mai, *loc. cit.*

the respective metals, selenophosphates of the alkali and alkaline earth metals and of magnesium can be prepared. The reaction takes place according to the equation:



The tetraselenophosphate is not obtained in the solid state, however, being decomposed by water, thus:



The decomposition may go still further, the compound $M_3PSe_2O_2$ or even M_3PSeO_3 being formed. Intermediate compounds such as $K_3PSe_{2.5}O_{1.5}$ are also formed, which may be isomorphous mixtures of various oxyselenophosphates.

The oxyselenophosphates may also be prepared by the action of phosphorus pentaselenide on the hydroxides of the metals. Normal salts are only obtained in the case of the alkali metals; the alkaline earth metals give monohydrogen salts. The following oxyselenophosphates have been prepared and described:¹

Sodium Trioxyselenophosphate, $Na_3PSeO_3 \cdot 20H_2O$, obtained by the action of phosphorus pentaselenide on either sodium hydroxide or sodium hydroselenide, crystallises in needles.

Ammonium Oxytriselenophosphate, obtained from phosphorus pentaselenide and a saturated solution of hydrogen selenide in strong ammonia, crystallises from the warm mother-liquor in leaflets having the composition $(NH_4)_3PSe_3O \cdot 10H_2O$. The cold mother-liquor afterwards deposits octahedra and four-sided leaflets having the composition $(NH_4)_5H(PSe_3O)_2 \cdot 18H_2O$.

Potassium Oxyselenophosphate, $K_3PSe_{2.5}O_{1.5} \cdot H_2O$, is obtained as greenish-yellow octahedra by using potassium hydroselenide.

Barium Dioxyselenophosphate, $BaHPSe_2O_2 \cdot 14H_2O$, formed when phosphorus pentaselenide is treated either with a solution of barium hydroxide or with a saturated solution of hydrogen selenide in barium hydroxide, is a white, microcrystalline powder.

Strontium Oxyselenophosphate, obtained as a light yellow precipitate by the action of phosphorus pentasulphide on strontium hydroxide and treatment of the filtrate with alcohol, has the composition $SrHPSe_3O_{1.7} \cdot 7H_2O$. Using a large excess of phosphorus pentaselenide the crystals obtained are colourless and have the composition $SrHPSe_3O_{1.8} \cdot 8H_2O$, which may possibly be $2SrHPSeO_3 \cdot SrHPSe_2O_2 \cdot 24H_2O$.

Calcium Oxyselenophosphate has been obtained in the same way, using calcium hydroxide instead of strontium hydroxide. With the smaller proportion of phosphorus pentaselenide the crystals have the composition $CaHPSe_3O_{1.5} \cdot 5H_2O$, whilst with the larger proportion their composition is $CaHPSeO_3 \cdot 8H_2O$.

A *magnesium dioxyselenophosphate* may also be obtained.¹

SELENIUM AND CARBON.

Carbon Diselenide, CSe_2 , has been produced in very small quantity by the action of carbon tetrachloride vapour on the selenide

¹ Ephraim and Majler, *Ber.*, 1910, 43, 285.

of phosphorus¹ or of cadmium² heated to dull redness. In the latter case a mixture of hexachloroethane, selenium chloride, selenium and traces of carbon diselenide, was obtained. The solution obtained by treating the mass with liquid carbon tetrachloride was shown by the addition of alcoholic potassium hydroxide to contain the diselenide, potassium selenoxanthate, KSe.CSe.OEt , separating as yellow needle-shaped crystals.

Carbon Subselenides of compositions C_4Se and C_5Se_2 have been described.³ When amorphous red selenium is distilled with carbon tetrabromide, in the molecular proportions 2 : 1, the greyish-black residue obtained after treatment with carbon disulphide, phenol, alcohol and ether in succession, has the composition $\text{C}_9\text{Br}_2\text{Se}_4$. This substance when heated with a very concentrated solution of sodium hydroxide forms the selenide C_4Se , a compound which dissolves with difficulty in concentrated sulphuric acid to give a light brown solution. If the sodium hydroxide solution of the bromoselenide is treated with hydrochloric acid, a violet-brown precipitate of the compound C_5Se_2 is obtained, which readily dissolves in hot concentrated sulphuric acid to give a reddish-brown solution.

The phenol extract of the residue from the foregoing distillation, on boiling with aqueous alcohol gives a brown, flocculent precipitate, of composition $\text{C}_{10}\text{BrSe}_6$, and this when boiled with concentrated sodium hydroxide also yields the selenide C_5Se_2 .

Other bromoselenides obtained by the interaction of selenium and carbon tetrabromide are stated to have the following compositions : $\text{C}_3\text{BrSe}_3 \cdot 8\text{H}_2\text{O}$, red crystals with a metallic lustre, m.pt. 120°C . ; $\text{C}_3\text{Br}_2\text{Se}_2$, orange-coloured solid, m.pt. 210° to 212°C . ; $\text{C}_2\text{Br}_2\text{Se}_4$, brownish-red leaflets, m.pt. 154°C .

Carbon Oxyselenide, COSe .—By the action of carbonyl chloride on cadmium selenide heated to redness, von Bartal⁴ obtained a gas which contained selenium and which was probably carbon oxyselenide. The gas did not liquefy at -80°C .

Carbon Sulphidoselenide, CSSe , may be prepared by the action of carbon disulphide vapour on ferrous selenide at 650°C . The product, on fractional distillation through a 50-inch bead-filled glass column, yields a deep yellow liquid as residue, which on repeated fractionation through the same column yields a middle fraction of the pure sulphidoselenide.⁵ It is obtained as a yellow oil of boiling-point 83.90° to 83.95°C . at 749.2 mm., and having a surface tension $\gamma = 40.44$ dynes/cm. at 20°C .

Under the action of zinc and hydrochloric acid the compound suffers reduction to hydrogen sulphide and hydrogen selenide. Chlorine reacts with it to form thiocarbonyl tetrachloride and selenium tetrachloride ; bromine acts analogously, except that under certain conditions the compound $\text{C}_2\text{S}_2\text{SeBr}_6$ may be formed.⁶ With ammonia the products of reaction are ill-defined.

¹ Rathke, *Annalen*, 1869, 152, 181.

² von Bartal, *Chem. Zeit.*, 1906, 30, 1044.

³ von Bartal, *ibid.*, p. 810.

⁴ von Bartal, *ibid.*, p. 1044.

⁵ Briscoe, Peel and Robinson, *J. Chem. Soc.*, 1929, p. 56 ; Stock and Willfroth, *Ber.*, 1914, 47, 144.

⁶ Briscoe, Peel and Robinson, *loc. cit.*, p. 1048.

Treatment with phenylhydrazine in alcohol solution yields the compound $(\text{NHPh.NH}_2)_2\text{CSSe}$, which appears to be a substituted sulphidoselenocarbamate analogous to the compound formed when phenylhydrazine reacts with carbon disulphide. It is an unstable substance with melting-point 98°C . Aniline yields a somewhat more stable compound $(\text{NHPh})_4\text{CSSe}$, with melting-point 164°C . With an alcoholic solution of sodium ethoxide, sodium monoselenoxanthate, NaS.CSe.OEt , is formed. This proves that the sulphidoselenide is analogous to carbon disulphide and carbon diselenide.

SELENIUM AND CYANOGEN.

Three cyanogen selenides have been described: cyanogen monoselenide or selenium dicyanide, $\text{Se}(\text{CN})_2$, cyanogen diselenide, selenocyanogen or selenious cyanide, $\text{Se}_2(\text{CN})_2$, and cyanogen triselenide, $\text{Se}_3(\text{CN})_2$.

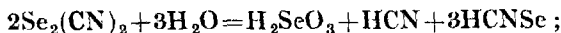
Cyanogen Monoselenide or Selenium Dicyanide, $\text{Se}(\text{CN})_2$, may be obtained by the action of silver selenocyanide, AgCNSe , on cyanogen iodide. Linnemann obtained it by the decomposition of silver cyanide with selenium bromide in carbon disulphide solution.¹ Cyanogen triselenide heated to 108°C . in a vacuum also yields the monoselenide.²

It consists of small tabular crystals which readily sublime. It is only slightly soluble in water, alcohol and ether; in chloroform and in carbon disulphide it is more soluble. It is decomposed by cold water into the triselenide, ammonium selenocyanate and selenious and hydrocyanic acids. Hot water decomposes it into selenious and hydrocyanic acids.³

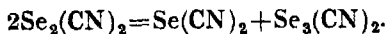
Cyanogen Diselenide or Selenocyanogen, $\text{Se}_2(\text{CN})_2$.—By heating together selenious anhydride, anhydrous hydrocyanic acid and acetic anhydride to 100°C . under pressure in a sealed tube until solution is complete, there are formed on evaporation of the product, yellowish crystals which have been regarded as impure cyanogen diselenide, $\text{Se}_2(\text{CN})_2$. On examination under the microscope these yellowish crystals appear as a mixture of brownish plates and needle-shaped crystals.⁴

The action of iodine on silver selenocyanate yields selenocyanogen.⁵ When potassium selenocyanate dissolved in anhydrous acetone reacts with a solution of lead tetra-acetate in chloroform, lead selenocyanate and selenocyanogen result.⁶

The diselenide has an intensely disagreeable smell and its vapours are very poisonous. It is hydrolysed by water thus:



the selenocyanic acid is only stable in neutral or alkaline solution. The diselenide is also readily decomposed by warm alcohol, and by dilute acids or alkalis. It undergoes polymerisation when heated in carbon disulphide solution, forming cyanogen mono- and tri-selenides:



¹ Linnemann, *Annalen*, 1849, 70, 47.

² Verneuil, *Ann. Chim. Phys.*, 1886, [6], 9, 289.

³ Verneuil, *loc. cit.*

⁴ Hinsberg, *Annalen*, 1890, 260, 40.

⁵ This reaction has been studied by Birckenbach and Kellermann, *Ber.*, 1925, 58, [B], 2377.

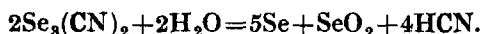
⁶ Kaufmann and Kogler, *Ber.*, 1926, 59, [B], 178.

Selenocyanogen may be identified¹ by conversion into diantipyryl selenide, $C_{22}H_{22}O_2N_4Se$, m.pt. $286^\circ C$.

Cyanogen Triselenide, $Se_3(CN)_3$, may be prepared by the action of a current of chlorine diluted with air on an aqueous solution of potassium selenocyanate, $KCNSe$. It may also be advantageously obtained by the action of nitric oxide on a paste of potassium selenocyanate with water.

It crystallises from water in needles which melt at $182^\circ C$. and decompose at $148.5^\circ C$. From chloroform solution it crystallises in golden-yellow tabular crystals. Some selenium is deposited from its ether and alcohol solutions. It is soluble in benzene and in carbon disulphide.

When acted on by hot water, cyanogen triselenide reacts according to the equation :



Calcium carbonate decomposes the triselenide thus :



The triselenide acts vigorously on many organic compounds with production of selenium, but the exact course of the reaction has not been ascertained in any one case as the products appear to be of a complex character.²

Selenocyanic Acid and the Selenocyanates.

Selenocyanic Acid, $HCNSe$, may be prepared in solution by decomposing the lead salt (obtained by treating potassium selenocyanate with lead acetate) with hydrogen sulphide.³ It is stable only in neutral or alkaline solution. *Selenocyanuric acid* has been obtained⁴ as a red amorphous powder by the action of cyanuric chloride on sodium selenide and subsequent precipitation by acids.

Ammonium Selenocyanate, NH_4CNSe , may be obtained by double decomposition between potassium selenocyanate and ammonium sulphate and subsequent digestion with alcohol. It is a fairly stable substance, analogous to the sulphur compound. It crystallises in minute needles which are soluble in water with absorption of heat.⁵

Cæsium Triselenocyanate, $Cs(CNSe)_3$, has been isolated⁶ as a reddish-brown salt, stable in air; it is soluble in alcohol, but decomposed by water.

Calcium, Strontium and Barium Selenocyanates have been prepared⁷ by dissolving the corresponding carbonates in selenocyanic acid and evaporating over sulphuric acid *in vacuo*. The calcium salt crystallises in groups of stellate crystals; the strontium salt separates out in well-defined prisms, while the barium salt is also crystalline.

Copper Selenocyanate is a brown precipitate obtained by precipitating copper sulphate with potassium selenocyanate. It is rapidly

¹ Kaufmann and Kögler, *Ber.*, 1926, 59, [B], 178.

² Verneuil, *Ann. Chim. Phys.*, 1886, [6], 9, 289; Muthmann and Schroder, *Ber.*, 1900, 33, 1765.

³ Stolte, *Ber.*, 1888, 19, 1577.

⁴ Stolte, *loc. cit.*

⁵ Cameron and Davy, *Chem. News*, 1881, 44, 63.

⁶ Birkenbach and Kellermann, *Ber.*, 1925, 58, [B], 2377.

⁷ Crookes, *Quart. J. Chem. Soc.*, 1852, 4, 19.

decomposed even at ordinary temperatures into black selenide of copper, with formation of hydrogen selenide.¹

Lead Selenocyanate has been obtained as a lemon-yellow compound by the action of lead acetate on potassium selenocyanate. It is soluble in boiling water but is slightly decomposed. The salt may be exposed without decomposition to a temperature of 100° C., but when moist assumes a pink tint.¹

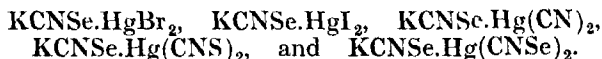
Magnesium Selenocyanate, $\text{Mg}(\text{CNSe})_2$, has been prepared by dissolving magnesium oxide in selenocyanic acid. On evaporation the salt is obtained as a gummy mass, apparently devoid of crystalline structure.²

Mercurous Selenocyanate, $\text{Hg}_2(\text{CNSe})_2$, can be obtained as an olive-green precipitate by the action of mercurous nitrate on potassium selenocyanate.³

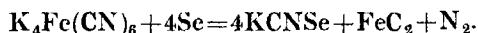
Mercuric Selenocyanate, $\text{Hg}(\text{CNSe})_2$, forms a crystalline mass when mercuric acetate is treated with potassium selenocyanate. The crystalline mass consists of white needles which are slightly soluble in cold water but readily soluble in alkali cyanide, thiocyanate and selenocyanate solutions. Mercuric selenocyanate turns brown in air and is decomposed by heat.⁴

A double compound $\text{Hg}(\text{CNSe})_2 \cdot \text{HgCl}_2$ has been obtained and described by Crookes. It consists of yellow crystals which are slightly soluble in cold water, more readily soluble in hot water. It is also very soluble in alcohol and in dilute hydrochloric acid, but it appears to decompose in the latter solvent, as the solution deposits selenium after standing for some time.⁵

The following double mercury compounds have been prepared and described by Cameron and Davy:⁶

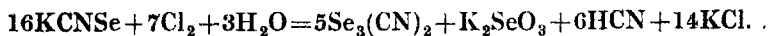


Potassium Selenocyanate, KCNSe .—Berzelius prepared this salt by the action of selenium on potassium ferrocyanide:⁷



By fusing pure potassium cyanide with selenium, Muthmann and Schröder obtained potassium selenocyanate satisfactorily.⁸

The salt crystallises in very deliquescent needles. The action of chlorine on its solution is complex, intermediate compounds being formed; the solution becomes dark red, some selenium is precipitated, and cyanogen triselenide is finally formed. The main reaction may probably be expressed by the equation:⁹



¹ Crookes, *loc. cit.*

² Berzelius, *Schweigger's J.*, 1821, 31, 60; Lassaigne, *J. Chim. Méd.*, 1840, [2], 6, 618; Crookes, *loc. cit.*

³ Cameron and Davy, *Chem. News*, 1881, 44, 63.

⁴ Cameron and Davy, *loc. cit.*

⁵ Crookes, *Annalen*, 1851, 78, 183.

⁶ Cameron and Davy, *loc. cit.*

⁷ Berzelius, *Traité de Chimie*, 1847, 3, 105.

⁸ Muthmann and Schröder, *Ber.*, 1900, 33, 1765.

⁹ Verneuil, *Compt. rend.*, 1886, 103, 144; *Bull. Soc. chim.*, 1884, 41, 18.

Iodine reacts with potassium selenocyanate in solution in the presence of much sodium bicarbonate according to the following equation:



By using excess of iodine and titrating after one hour with sodium thio-sulphate in the presence of a little carbon disulphide, the reaction may be used for the determination of the selenocyanate.¹

A double selenocyanate of potassium and platinum may be obtained by mixing alcohol solutions of potassium selenocyanate and either platinum tetrachloride or chloroplatinic acid.² The double salt, *potassium platiseleocyanate*, $\text{K}_2\text{Pt}(\text{CNSe})_6$, consists of hexagonal plates, density 3.877 at 10.2° C., dark red by transmitted light and black by reflected light. The gold salt, $\text{KAu}(\text{CNSe})_2$, is obtained in a similar manner and consists of very easily decomposable dark red prisms.

Silver Selenocyanate, AgCNSe , is obtained as a white precipitate closely resembling silver chloride by the action of silver nitrate on a solution of potassium selenocyanate. If, however, ammonia is previously added in excess to the silver nitrate solution, the selenocyanate is precipitated in minute satin-like crystals.

Silver selenocyanate is readily blackened by the action of light. It is insoluble in water and only very sparingly soluble in ammonia and cold dilute acids. It is decomposed by boiling concentrated acids with the deposition of selenium, unless the acid used has oxidising properties.

Sodium Selenocyanate, NaCNSe .—By neutralising selenocyanic acid with sodium hydroxide and evaporating the solution *in vacuo*, small foliated crystals of sodium selenocyanate are obtained. Sodium selenocyanate is very soluble in water, giving an alkaline reaction.³

Zinc Selenocyanate may be obtained by dissolving either the metal or its oxide in selenocyanic acid. It forms groups of prismatic needles, which are not deliquescent.⁴ By the action of selenium on a solution of zinc cyanide in liquid ammonia, the compound $\text{Zn}(\text{CNSe})_2 \cdot 4\text{NH}_3$ has been obtained.⁵ Similar compounds of magnesium and aluminium have also been described.

SELENIUM AND SILICON.

Silicon Selenide, SiSe_2 .—When crystalline silicon is heated to a red heat in a current of dry hydrogen selenide reaction takes place with the formation of silicon selenide; ⁶ the product is a dark, variegated mass, of metallic appearance, and has a very irritating odour. When heated to a dull red heat in a current of air or oxygen it undergoes oxidation with the formation of selenium, but the reaction is only superficial. Water reacts vigorously with the selenide with the production of silica and the liberation of hydrogen selenide. The silica forms a protective coating which hinders the total decomposition of the selenide. The reaction is more complete in the presence of caustic potash, which dissolves both the silica and the hydrogen selenide.

¹ Kaufmann and Kögler, *Ber.*, 1926, 59, [B], 178.

² Clarke and Dudley, *ibid.*, 1878, 11, 1325.

³ Crookes, *Annalen*, 1851, 78, 177.

⁴ Crookes, *J. Chem. Soc.*, 1852, 4, 19.

⁵ Bergstrom, *J. Amer. Chem. Soc.*, 1926, 48, 2319.

⁶ Sabatier, *Compt. rend.*, 1891, 113, 172.

. SELENIUM AND BORON.

When iron or manganese boride is heated in selenium vapour the product obtained is contaminated with a yellowish-grey substance which is *selenium boride*, B_2Se_3 .¹ This has also been obtained² by directing either selenium vapour or a current of hydrogen selenide gas on to red-hot boron. Selenium boride is a yellow solid which gives an irritating odour of hydrogen selenide when exposed to moist air, some boric acid being formed at the same time.

¹ Hoffmann, *Chem. Zeit.*, 1911, 35, 713.

² Sabatier, *Compt. rend.*, 1891, 112, 1000.

CHAPTER VI.

TELLURIUM.

Symbol, Te. Atomic weight, 127.5.

Occurrence.—Tellurium occurs to a relatively small extent in nature and is only found in certain localities, more particularly in Hungary (Transylvania)¹ and in the United States (especially Colorado).² It occurs in smaller quantity in various parts of South America, *e.g.* in Bolivia,³ Brazil and Chile, also in Mexico,⁴ Honduras,⁵ Australia⁶ and Asia Minor.⁷

In the native condition the element is occasionally found as hexagonal prismatic crystals, which are nearly pure. The foreign metals present, usually only in small quantity, may be gold, silver, copper and iron. Free tellurium is also present to the extent of approximately 0.17 per cent. in the red sulphur of Japan, which also contains about 6 per cent. of selenium and 1 per cent. of arsenic.⁸ Traces of tellurium may be found in Spanish pyrites.⁹

The element occurs most frequently as telluride, the accompanying metal being variable. The better known natural tellurides include those of nickel (*melonite*, Ni_2Te_3), bismuth (*tetradymite*, which also contains sulphur, $\text{Bi}_2\text{Te}_2\text{S}$, and *joseite*, of similar qualitative composition), lead (*altaite*, PbTe), mercury (*coloradoite*, HgTe), silver (*hessite*, Ag_2Te) and gold (*calaverite*, AuTe_2).

In addition to the tellurides of simple composition, double tellurides are known; *e.g.* *sylvanite* (graphic tellurium) and *petzite*, gold-silver tellurides. Even more complex mixtures occur, *e.g.* the Australian *coolgardite* and *calgoorlite*, which are mixtures of several simpler tellurides and contain tellurium, mercury, silver and gold.¹⁰ The mineral *nagyagite*, also known as "leaf tellurium," approximates in composition to $(\text{AuPb})_2(\text{TeSSb})_3$.

Tellurium oxide, TeO_2 , is found in rhombic crystals as the mineral *tellurite*, whilst *ferrotellurite* is probably an iron tellurate, *emmonsite* and *dividensite* being similar compounds. Other naturally occurring tellurates are *montanite*, a basic bismuth tellurate, and *magnolite*, a

¹ Petz, *Ann. Phys. Chem.*, 1842, [n.], 57, 467; Muthmann and Schroder, *Zeitsch. Kryst. Min.*, 1897, 29, 140.

² Egleston, *Chem. News*, 1883, 47, 51; Vincent, *Bull. Soc. chim.*, 1902, [iii.], 27, 23; Rolland, *Ann. Mines*, 1878, [vii.], 13, 159, 200.

³ Schneider, *J. prakt. Chem.*, 1881, [ii.], 23, 78.

⁴ Domeyko, *Compt. rend.*, 1875, 81, 632; de Londero, *Zeitsch. Kryst. Min.*, 1887, 13, 320.

⁵ Dana and Wells, *Amer. J. Sci.*, 1890, [ii.], 40, 78, 82.

⁶ *Abstr. Chem. Soc.*, 1898, 74, ii., 385; MacIvor, *Chem. News*, 1900, 82, 272.

⁷ Cesaro, *Bull. Acad. roy. Belg.*, 1908, p. 255.

⁸ Divers and Shimidzu, *Chem. News*, 1883, 48, 284; Divers and Shimosé, *ibid.*, 1881, 44, 229; 1884, 49, 26.

⁹ Playfair, *Chem. News*, 1879, 39, 245.

¹⁰ Liveing, *Eng. and Min. J. (New York)*, 1908, 75, 814.

mercurous tellurate. *Arsenotellurite* contains tellurium, arsenic and sulphur.¹

Early History.—The existence of tellurium was first indicated at the beginning of 1788 by Müller of Hermannstadt, whose experiments suggested that the mineral known as *aurum paradoxum* (an auriferous native tellurium) contained a new element. Bergmann of Upsala in 1788 concluded that a new element had actually been isolated. In 1789 the element was discovered independently by Kitaibel, and this discovery was confirmed in 1798 by Klaproth of Berlin, who suggested the name tellurium (Lat., *tellus*, the earth).² A systematic examination of the chemical behaviour and characteristics of the new element was first carried out by Berzelius in 1835.³

Extraction.—The processes which have been used for the extraction of tellurium from its minerals and from the residues obtained from the metallurgical treatment of telluriferous ores of other metals, are relatively numerous, a different procedure having been adopted in almost every case. In effect, however, the principles involved are few. The tellurium may be obtained as alkali telluride by heating with alkali carbonate and a reducing agent, when the aqueous solution can be submitted to atmospheric oxidation, with liberation of the tellurium.⁴ This method, usually followed for bismuth telluride ores, resembles in some respects the method of treatment of mixtures containing free tellurium; e.g. "chamber mud," from Japanese sulphur, is extracted with alkaline potassium cyanide solution, the resulting solution of unstable potassium tellurocyanide on treatment with hydrogen sulphide giving a deposit of tellurium sulphide; this deposit can again be converted into potassium tellurocyanide by fusion with potassium cyanide and the tellurium then separated by atmospheric oxidation of the solution.⁵

On the other hand, especially in the case of the gold and silver ores, a process of oxidation may be applied. Oxidation may be effected by fusion with a mixture of potassium nitrate and alkali carbonate,⁶ by the action of aqua regia⁷ or even by merely heating with concentrated or fuming sulphuric acid.⁸ The last-named reagent, in the form of oleum containing 20 per cent. SO_3 , is now generally applied for the extraction of tellurium from *hessite*-bearing ore, the earthy mineral containing 4 to 5 per cent. of silver telluride, which constitutes one of the two most important sources of commercial tellurium, the other source being the "anode mud" of the copper refineries.⁹ After oxidation, water is added, and silver, the main product of the extraction, is precipitated by the addition of hydrochloric acid. The aqueous solution of the resulting tellurous or telluric acid is then heated with a reducing agent, sulphurous acid being frequently applied, although metals such as zinc may be used,¹⁰ the tellurium being precipitated.¹¹ If aqua regia

¹ Hannay, *Trans. Chem. Soc.*, 1873, 26, 989.

² Klaproth, *Crell's Annalen*, 1798, 1, 91, Durgart, *Zeitsch. angew. Chem.*, 1920, 33, 299.

³ Berzelius, *Ann. Chim. Phys.*, 1835, 58, 113, 150, 225; *Ann. Phys. Chem.*, 1833, 28, 392; 1834, 32, 1, 577. These papers give a general account of Berzelius' investigations on tellurium.

⁴ See Becker, *Annalen*, 1876, 180, 257.

⁵ Shimosé, *Chem. News*, 1884, 49, 26.

⁶ Berthier, *Ann. Chim. Phys.*, 1832, 51, 156.

⁷ Schrötter, *Ber.*, 1876, 6, 552.

⁸ Farbaky, *Zeitsch. angew. Chem.*, 1897, 11, 18.

⁹ See Dyson, *Chemical Age*, 1928, 19, Met. Sect., p. 17.

¹⁰ Löwe, *J. prakt. Chem.*, 1853, 60, 163.

¹¹ See also Hulot, *Bull. Soc. chim.*, 1921, [iv.], 29, 1070.

has been used as the oxidising agent, gold is first removed by means of ferrous sulphate and oxalic acid.

The "anode mud" is now a much more important source of tellurium than any of the minerals. The mud is generally roasted in a current of air, when tellurium dioxide is formed. This condenses, together with oxides of arsenic and antimony, as small white crystals in the flues and cooling chambers, and is reduced to tellurium by smelting with charcoal at a low temperature.¹

The crude product from any of the foregoing processes usually contains from 70 to 85 per cent. of tellurium.

Purification.—Taking into account its relatively small practical importance, no element has had more time or thought devoted to its purification than has tellurium. This arises largely from the unexpected position of its atomic weight amongst the corresponding figures for the other elements. The variation in the results obtained supplies good evidence that the entire removal of impurities is a difficult task.²

Different types of methods for purification have been applied. Brauner in 1889, by means of aqua regia, converted crude tellurium into telluric chloride, the aqueous solution of which on precipitation by sulphur dioxide deposited the element together with selenium and traces of copper and lead as the only impurities.³ The precipitate was dissolved in fused potassium cyanide in an atmosphere of hydrogen and the tellurium separated from the aqueous extract by treatment with a current of air. The element was then distilled in a current of hydrogen;⁴ an alternative is distillation in a vacuum.⁵ Another method of treatment for the telluric chloride solution is to precipitate in three fractions using sulphur dioxide, when it is found that the middle fraction is of a high degree of purity.⁶

Another group of methods involves the conversion of the tellurium into some compound, inorganic or organic, which can be purified and then made to regenerate the element. Hydrogen telluride,⁷ crystalline telluric acid,⁸ basic tellurium nitrate⁹ and diphenyl telluride¹⁰ have all been made use of.

Under suitable current conditions, tellurium may be deposited electrolytically in a very pure form from sulphuric acid solution.

Physical Properties.—Tellurium is known in amorphous and crystalline forms, but it appears to differ from sulphur and selenium in

¹ For the recovery of tellurium from copper residues, see Whitehead, *J. Amer. Chem. Soc.*, 1895, 17, 849, 855; Lenher, *ibid.*, 1899, 21, 347, 351; Keller, *ibid.*, 1897, 19, 771; Crane, *Amer. Chem. J.*, 1900, 23, 408; Oberhelman and Browning, *Amer. J. Sci.*, 1913, [iv.], 36, 399; from gold residues, Crane, *Amer. Chem. J.*, 1900, 23, 435; from bismuth residues, Matthey, *Proc. Roy. Soc.*, 1901, 68, 161.

² Baker and Bennett, *Trans. Chem. Soc.*, 1907, 91, 1849; Marckwald, *Ber.*, 1907, 40, 4730; Harcourt and Baker, *Trans. Chem. Soc.*, 1911, 99, 1311; Browning and Flint, *Amer. Chem. J.*, 1909, 28, 347; Flint, *J. Amer. Chem. Soc.*, 1912, 34, 1325; Morgan, *ibid.*, 1912, 34, 1669; Lenher, *ibid.*, 1908, 30, 741; Schelle, *Seventh Intern. Congr. Appl. Chem.*, 1909, [iii.], A, 80.

³ Brauner, *Trans. Chem. Soc.*, 1889, 55, 411.

⁴ See also Becker, *Annalen*, 1876, 180, 257.

⁵ Schuller, *Ann. Phys. Chem.*, 1883, [iii.], 18, 317. See also Kahlbaum, Roth and Siedler, *Zeitsch. anorg. Chem.*, 1902, 29, 177; Krafft and Merz, *Ber.*, 1903, 36, 4344.

⁶ Köthner, *Annalen*, 1901, 319, 15.

⁷ Ditte, *Ann. Sci. École Norm.*, 1872, [ii.], 1, 193.

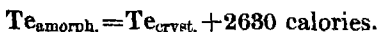
⁸ Staudenmaier, *Zeitsch. anorg. Chem.*, 1896, 10, 189.

⁹ Norris, Fay and Edgerly, *Amer. Chem. J.*, 1900, 23, 105.

¹⁰ Steiner, *Ber.*, 1901, 34, 570.

that it yields only one variety of each form. It may also be obtained in colloidal solution.

Amorphous Tellurium is a brownish-black powder usually obtained by precipitation methods, for example by reducing a solution of tellurium dioxide with sulphurous acid.¹ On heating it is transformed into crystalline tellurium with development of heat :



It resembles the crystalline variety in behaviour except in such properties as are influenced by its fineness of division. The electrometric properties of the two forms are identical.² The density of the amorphous form ranges from 5.85 to 5.87 ; ³ the specific heat is 0.052.⁴

Crystalline Tellurium.—Molten tellurium solidifies to a brittle, silvery, crystalline mass, which is easily powdered. The crystalline modification can also be obtained by sublimation of the element or by its slow formation, for example in the gradual decomposition of hydrogen telluride⁵ or in the slow atmospheric oxidation of an aqueous solution of an alkali telluride.⁶ When obtained of appreciable size the crystals are generally found to be prismatic, of the trigonal system, and isomorphous with "metallic" selenium ($a : c = 1 : 1.3298$; $\alpha = 86.8^\circ$).⁷

The density of crystalline tellurium is curiously variable, the mass obtained after fusion having a density about 6.24, whilst distilled or precipitated tellurium generally gives a lower value, usually 6.15 to 6.23.⁸ According to Cohen and Kröner⁹ the density alters under the influence of heat, and this, together with other inconstancies, is attributed to the presence of two dynamic allotropes in ordinary tellurium, the density as well as the other physical properties depending on the relative proportions. This view is not supported, however, by the more recent work of Damiens,¹⁰ in which the tellurium used had been carefully purified by successive distillation in hydrogen and *in vacuo*, followed by crystallisation either by vaporisation or by slow cooling of the molten material. The density of the tellurium obtained by vaporisation was found to be 6.310, and this value did not alter on heating. Specimens prepared in other ways were slightly porous and consequently had a slightly lower density.¹¹

The compressibility of tellurium at 25° C. between 100 and 500 megabars¹² is 5.00×10^{-6} per megabar, a value which falls on the smooth compressibility - atomic volume curve for the elements.¹³

¹ Beljankin, *J. Russ. Phys. Chem. Soc.*, 1901, 33, 670.

² Schuhmann, *J. Amer. Chem. Soc.*, 1925, 47, 356.

³ Damiens, *Compt. rend.*, 1922, 174, 1344, 1548. Beljankin, however, gives 6.02 at 20° C.

⁴ Regnault, *Ann. Chim. Phys.*, 1836, [2], 62, 364 ; Fabre, *ibid.*, 1887, [6], 14, 101.

⁵ Ditte, *Compt. rend.*, 1872, 74, 980.

⁶ Beljankin, *loc. cit.*

⁷ Rose, *Ann. Phys. Chem.*, 1849, [ii.], 77, 146 ; also Kahlbaum, *Zeitsch. anorg. Chem.*, 1902, 29, 288.

⁸ Klein and Morel, *Ann. Chim. Phys.*, 1885, [vi.], 5, 61 ; Beljankin, *loc. cit.* ; Fay and Gillson, *Amer. Chem. J.*, 1902, 27, 81 ; Kahlbaum, Roth and Siedler, *Zeitsch. anorg. Chem.*, 1902, 29, 289.

⁹ Cohen and Kroner, *Zeitsch. physikal. Chem.*, 1913, 82, 587.

¹⁰ Damiens, *Compt. rend.*, 1922, 174, 1344, *Ann. Chim.*, 1922, [ix.], 18, 282.

¹¹ The tensile strength of large single crystals of tellurium has been determined ; see Schmid and Wassermann, *Zeitsch. Physik*, 1928, 46, 653.

¹² 1 megabar = 0.987 atm. at sea-level, 45° latitude.

¹³ Mehl and Mair, *J. Amer. Chem. Soc.*, 1927, 49, 1892.

Tellurium melts at 452°C.^1 and boils near 1890°C. under ordinary pressure,² but volatilises at as low a temperature as 480°C. in a cathode-ray vacuum; the vapour is yellow in colour.³ Like the density, the specific heat of the solid is inconstant, ranging from 0.0475 for the distilled element to 0.0524 for the precipitated amorphous substance.⁴ It has been observed⁵ that exposure to X-rays increases the specific heat of tellurium by about 8 per cent., possibly owing to a change in the structure of the element.

Solid tellurium is a bad conductor of heat and electricity;⁶ a maximum value for the electrical resistance has been observed and placed at 50° to 140°C. by different investigators.⁷ The occurrence of this maximum has also been attributed to the presence of two dynamic allotropic forms. At higher temperatures, above 800°C. , the specific resistance decreases exponentially with rise in temperature.⁸

Liquid tellurium is comparatively a good conductor of electricity, the specific conductance at the freezing-point being about 15 times that of the solid, whilst at 500°C. it is equal to one-sixth of that of mercury at the ordinary temperature.⁹

Tellurium shows a higher resistance towards an alternating current of high frequency than towards a direct current.¹⁰ Exposure to light causes a very slight increase in the electrical conductivity,¹¹ the effect being very much less than that produced with selenium.

The "Hall effect," *i.e.* the displacement of the equipotential lines when a current flows along a thin strip of metal placed between the poles of a magnetic field, is greater in the case of tellurium than for any other metal, the constant being $+530$.¹² Tellurium is diamagnetic, its susceptibility being ¹³ -0.32×10^{-6} , a value which varies only slightly with the temperature but falls suddenly at the melting-point.

The linear coefficient of expansion of tellurium at the ordinary temperature is 0.0000344.¹⁴ The latent heat of fusion at 446°C. is 33.50 gm. cal.¹⁵

Molten tellurium dissolves many metals and its cryoscopic constant

¹ Šimek and Stehlik, *Brit. Chem. Abs.*, 1930, A, 986, Carnelley and Williams, *Trans. Chem. Soc.*, 1880, 37, 125; Matthey, *Proc. Roy. Soc.*, 1901, 68, 161.

² Deville and Troost, *Compt. rend.*, 1880, 91, 83.

³ Krafft and others, *Ber.*, 1903, 36, 1690, 4344.

⁴ Regnault, *Ann. Chim. Phys.*, 1856, [iii.], 46, 257; Fabre, *ibid.*, 1887, [vi.], 14, 101.

⁵ Adinolfi, *Atti R. Accad. Lincei*, 1928, [vi.], 8, 381.

⁶ Matthiessen, *Ann. Phys. Chem.*, 1858, [ii.], 103, 431; Lenher and Morgan, *J. Amer. Chem. Soc.*, 1900, 22, 28.

⁷ Matthiessen, *Ann. Phys. Chem.*, 1862, [ii.], 115, 385; Tibbals, *J. Amer. Chem. Soc.*, 1909, 31, 902; Haken, *Ann. Physik*, 1910, [4], 32, 291.

⁸ Kraus and Johnson, *J. Physical Chem.*, 1928, 32, 1281.

⁹ The specific resistance of mixtures of tellurium with up to 85 atoms per cent. of sulphur has been measured over the temperature range 382° to 477°C. by Kraus and Johnson, *loc. cit.*

¹⁰ Geipel, *Ann. Physik*, 1912, [4], 38, 149.

¹¹ Adams, *Ann. Phys. Chem.*, 1876, [ii.], 159, 629.

¹² Collet, *Compt. rend.*, 1913, 156, 943. For a study of the "Hall effect" in sputtered tellurium films, see Warburton, *Phys. Review*, 1927, [ii.], 30, 673.

¹³ Honda, *Ann. Physik*, 1910, [4], 32, 1027; Endo, *Sci. Rep. Tôhoku Imp. Univ.*, 1927, 16, 201.

¹⁴ Spring, *Bull. Acad. roy. Belg.*, 1881, [iii.], 2, 88. This value is double that obtained by Fizeau, *Compt. rend.*, 1869, 68, 1125.

¹⁵ Umino, *Kinzoku no Kenku*, 1926, 3, 498. This author also gives the heat of a molecular transformation at 348°C. as 0.63 gm. cal.

has been found to have a value between 510 and 585.¹ Tellurium itself dissolves in pyrosulphuric acid, and freezing-point determinations show that it is present in this solution as monatomic molecules² (cf. p. 357).

The optical constants—refractive indices, reflecting powers and absorption constants—of isolated crystals of tellurium placed in various positions relative to the plane of incidence have been determined³ for wave-lengths of 3000 to 5000 Å. The absorption of light by tellurium vapour reaches a maximum at 1200° C.⁴

Vapour density determinations show that tellurium is diatomic at high temperatures (about 1500° C.),⁵ whilst at 2100° C. considerable dissociation into single atoms has taken place. According to Jouniaux⁶ the element is monatomic at 357° C. At lower temperatures, as in the case of sulphur and selenium, the molecule is more complex. The vapour pressure of tellurium has been determined⁷ and is as follows:

t (° C.)	488	578	671
p (atm.)	$6 \cdot 10 \times 10^{-4}$	$4 \cdot 40 \times 10^{-3}$	$1 \cdot 86 \times 10^{-2}$

and the mean value for the heat of volatilisation has been calculated to be 26.5 cal. per gm. mol.

Colloidal Tellurium.—On reduction of dilute solutions of tellurium dioxide or telluric acid by means of hydrazine, hydroxylamine, hypophosphorous acid, sulphurous acid or salts of these compounds, brown or blue colloidal solutions can be obtained, the stability of which is greatly increased by the presence of an organic colloid such as gum arabic, sodium lysalbate or sodium protalbate.⁸ Similarly the addition of an extract of the seeds of *Plantago psyllium*, in amount not exceeding 0.3 per cent., renders extremely stable the sols obtained by the reduction of telluric acid with hydrazine hydrate.⁹ Stable sols may also be obtained by the reduction of telluric acid with dextrose in the presence of ammonia. Dialysis does not completely remove the adsorbed dextrose and this undoubtedly contributes to the remarkable stability.¹⁰ The particles of colloidal tellurium in these sols are negatively charged.

Tellurium in a very finely divided condition may be obtained by mixing aqueous solutions of dextrose (30 per cent.) and sodium tellurite (5 per cent.) and heating to boiling for half an hour.¹¹

Various other methods of preparing colloidal tellurium have been described. If a small quantity of the element is dissolved in a boiling solution of potassium hydroxide and the product poured into a large bulk of cold water with vigorous stirring, tellurium remains in colloidal solution.¹² Colloidal aqueous solutions have also been produced by

¹ Pélabon, *Ann. Chim. Phys.*, 1909, [viii.], 17, 536; *Compt. rend.*, 1908, 146, 1397.

² Auerbach, *Zeitsch. physikal. Chem.*, 1926, 121, 337; *Kolloid-Zeitsch.*, 1926, 38, 343.

³ Miller, *J. Opt. Soc. Amer.*, 1925, 10, 621; Sieg and van Dyke, *Phys. Review*, 1923, 21, 206; Sieg, *ibid.*, p. 211.

⁴ Dobbie and Fox, *Proc. Roy. Soc.*, 1920, [A], 98, 147.

⁵ von Wartenberg, *Zeitsch. anorg. Chem.*, 1907, 56, 320; Dobbie and Fox, *loc. cit.*; Jouniaux, *Bull. Soc. chim.*, 1924, [iv.], 35, 1607. ⁶ Jouniaux, *loc. cit.*

⁷ Doolan and Partington, *Trans. Faraday Soc.*, 1924, 20, 342.

⁸ Guthier, *Zeitsch. anorg. Chem.*, 1902, 32, 51, 91; Guthier and Resenscheck, *ibid.*, 1904, 42, 177; Paal and Koch, *Ber.*, 1905, 38, 534.

⁹ Guthier, Huber and Eckert, *Kolloid-Zeitsch.*, 1923, 32, 329.

¹⁰ Guthier and Ottenstein, *Zeitsch. anorg. Chem.*, 1925, 149, 223.

¹¹ Levaditi, *French Patent*, 626506 (1926).

¹² von Weimarn and Maljischeff, *J. Russ. Phys. Chem. Soc.*, 1910, 42, 484.

the cathodic pulverisation of tellurium under water,¹ and by the electrolysis of an aqueous solution of telluric acid containing either potassium cyanide or ammonium oxalate.²

The presence of colloidal tellurium in glass produces a colour tint which varies from blue to brown according to the size of the colloid particles, the blue glass containing larger particles than the brown.³ Polytellurides are present in some coloured glasses and impart a colour which is red or violet-red.

The coagulating powers of various electrolytes for tellurium hydrosols have been determined;⁴ the results obtained do not agree with Whetham's law.

*Spectrum.*⁵—The arc and spark spectra of tellurium have been investigated, the arc being produced in an atmosphere of carbon dioxide between tellurium electrodes or between carbon electrodes one of which carried pieces of tellurium in a small cavity. Fifteen distinctive lines between 3175 and 2081 Å⁶ and forty of wave-length less than 2080 Å⁷ have been measured. The most prominent lines are: 2142·75, 2259·02, 2383·24, 2385·76, 2769·65 and 3175·13 Å. The lines at 2769·65 and 3175·13 have been shown to be distinct from those of antimony (2769·94) and tin (3175·04) by photographing the spectra of mixtures of these elements with tellurium, when in each case the two separate lines were obtained.⁸

The non-luminous vapour of tellurium absorbs the lines 2081, 2143, 2147, 2209, 2259, 2383 and 2386 Å. At 1600° C. the vapour, presumed to contain some monatomic tellurium (see p. 355), absorbs the lines 2143 and 2259 Å, but according to Kimura⁹ not 2383 and 2386 Å,¹⁰ so that the latter lines probably originate in transitions involving metastable states. In the ultra-violet region, tellurium vapour shows eleven wave-lengths absorbed between 2000 and 1650 Å.¹¹

When illuminated by an incandescent gas lamp, tellurium vapour exhibits an intense bluish-green fluorescence. Under the light of a mercury vapour lamp the fluorescence is much less intense. The fluorescence spectrum consists of regularly spaced bands in the visible region.¹²

¹ Müller and Lucas, *Zeitsch. Elektrochem.*, 1905, **11**, 521.

² Guthrie and Resenscheck, *Zeitsch. anorg. Chem.*, 1904, **40**, 264.

³ Fenaroli, *Chem. Zest.*, 1914, **38**, 873; *Kolloid-Zeitsch.*, 1915, **16**, 53.

⁴ Doolan, *J. Physical Chem.*, 1925, **29**, 178.

⁵ For various spectrographic researches on tellurium, see Thalen, *Ann. Chim. Phys.*, 1869, [iv.], **18**, 244; Salet, *Compt. rend.*, 1871, **73**, 742; Hartley, *Proc. Roy. Soc.*, 1883, **35**, 148; de Gramont, *Compt. rend.*, 1898, **127**, 866, 868; Grünwald, *Monatsh.*, 1889, **10**, 829; Ditte, *Compt. rend.*, 1871, **73**, 622; Dudley and Jones, *J. Amer. Chem. Soc.*, 1912, **34**, 995; Patterson, *Amer. J. Sci.*, 1913, [iv.], **36**, 135; Siegbahn, *Ber. Deut. physikal. Ges.*, 1916, **18**, 39; McLennan, Smith and Peters, *Trans. Roy. Soc. Canada*, 1925, [iii.], **19**, III., 39; Nagaoka, Nukiya and Futagami, *Proc. Imp. Acad. Tokyo*, 1927, **3**, 409; Lang, *Proc. Nat. Acad. Sci.*, 1927, **13**, 341; Bloch and Bloch, *Compt. rend.*, 1927, **185**, 761; 1928, **187**, 562; Allin, *Trans. Roy. Soc. Canada*, 1927, [iii.], **21**, III., 231; Lacroute, *J. Phys. Radium*, 1928, [vi.], **9**, 180.

⁶ Uhler and Patterson, *Amer. J. Sci.*, 1913, [iv.], **36**, 135.

⁷ McLennan, McLay and McLeod, *Phil. Mag.*, 1927, [vii.], **4**, 486.

⁸ Uhler and Patterson, *loc. cit.*

⁹ Kimura, *Japan J. Phys.*, 1927, **4**, 81.

¹⁰ Cf. Zumstein, *Phys. Review*, 1926, [ii.], **27**, 562.

¹¹ McLennan and Cooley, *Trans. Roy. Soc. Canada*, 1926, [iii.], **20**, III., 349.

¹² Rakowicz-Pogorzelska, *Bull. Inter. Acad. Polonaise*, 1926, **A**, 243; McLennan and Walerstein, *Phys. Review*, 1927, [ii.], **29**, 208; McLennan, Walerstein and Grayson Smith, *Phil. Mag.*, 1927, [vii.], **3**, 390. See also Steubing, *Physikal. Zeitsch.*, 1913, **14**, 887; Diestelmeier, *Zeitsch. wiss. Photochem.*, 1915, **15**, 18; Rosen, *Zeitsch. Physik*, 1927, **43**, 69.

Chemical Properties.—In spite of its definite metallic tendencies, tellurium shows considerable similarity in its chemical behaviour to sulphur and selenium. Its activity is, however, much less marked, and in general the compounds formed are less stable than their sulphur and selenium analogues.

At high temperatures tellurium combines directly, but only to a small extent, with hydrogen, forming hydrogen telluride.¹

In a fine state of division the element is not acted on by atmospheric oxygen, but above its melting-point it burns with a green-bordered blue flame, giving the dioxide, even in the driest oxygen.²

Water is without effect on the element even at a red heat,³ but the combined action of water and ozone produces telluric acid at the ordinary temperature.⁴ The action of hydrogen peroxide upon tellurium is influenced considerably by the physical state of the element; colloidal tellurium is readily oxidised, but crystalline tellurium is not readily attacked and has first to be dissolved in an aqueous solution of alkali hydroxide, when oxidation becomes possible with formation of tellurate.⁵ Hydrogen peroxide of 60 per cent. strength reacts very slowly with tellurium at a temperature of 100° C., but with increasing amount of telluric acid formed, the rate of dissolution increases. Amorphous tellurium as ordinarily prepared behaves in a similar manner to the crystalline variety, but if it is dried by treatment with alcohol and ether instead of by heating at 105° C. it will dissolve readily in a concentrated solution of hydrogen peroxide.⁶

Nitric acid oxidises tellurium only to the stage of the dioxide.⁷ Under certain conditions, using large quantities of material and a high column of liquid, tellurium nitrite may be obtained as a flesh-coloured precipitate which can be dried at 100° C. without decomposition; at higher temperatures decomposition sets in, leaving a yellow residue of tellurium dioxide.⁸

Sulphuric acid dissolves the element to form a red solution, the colour being due possibly to sulphur-tellurium sesquioxide, STeO_3 , which has not been isolated.⁹ On warming, tellurium dioxide and sulphur dioxide are produced. If the sulphuric acid is hot and concentrated, a red solution is obtained from which tellurium may be separated by the addition of water. This solution is similar to that obtained with pyrosulphuric acid, in which Auerbach has shown that the tellurium is present in monatomic form (see p. 355). If the red solution is boiled for some time, white crystals of pyrotelluric sulphate, $2\text{TeO}_2 \cdot \text{SO}_3$, separate. These crystals are soluble in hydrochloric acid and decompose on heating with water.¹⁰ A red solution is also obtained with cold anhydrous selenic acid and presumably contains the corresponding selenium-tellurium sesquioxide, SeTeO_3 .¹¹

¹ Löwe, *J. prakt. Chem.*, 1853, 60, 165; Becker, *Annalen*, 1876, 180, 258; Brauner, *Monatsh.*, 1889, 10, 416. See also Gutbier, *Zeitsch. anorg. Chem.*, 1902, 32, 31.

² Gutbier, *loc. cit.*

³ Cross and Higgin, *Trans. Chem. Soc.*, 1879, 35, 249.

⁴ Mailfert, *Compt. rend.*, 1882, 94, 1186.

⁵ Gutbier and Resenschek, *Zeitsch. anorg. Chem.*, 1904, 42, 174.

⁶ Schluck, *Monatsh.*, 1916, 37, 489.

⁷ Gutbier, *Zeitsch. anorg. Chem.*, 1902, 32, 31.

⁸ Oefele, *Pharm. Zentr.-h.*, 1920, 61, 491.

⁹ Divers and Shimosé, *Ber.*, 1883, 16, 1008.

¹⁰ Gutbier, *loc. cit.*

¹¹ Cameron and Macallan, *Proc. Roy. Soc.*, 1889, 46, 31.

All the halogen elements combine with tellurium. The powdered crystalline form is inflamed by fluorine in the cold¹ and by warm chlorine, the product in the latter case being the tetrachloride.² With bromine the product is the dibromide, whilst iodine reacts only at a higher temperature, giving a tetra-iodide. Hydrogen chloride does not affect the element.

Pyrosulphuryl chloride, sulphuryl chloride, thionyl chloride and sulphur monochloride all convert tellurium into the tetrachloride, the reaction proceeding most readily with the last named. In the case of thionyl chloride and sulphur monochloride the product is tellurium dichloride if the tellurium is present in excess.³ With pyrosulphuryl chloride the compound formed is $\text{TeCl}_4 \cdot \text{SO}_3$; when this is acted upon by dry ammonia the product contains tellurium nitride.⁴

Combination takes place between many metals and molten tellurium. By examination of the freezing-point curve for mixtures of the metal and tellurium in varying proportions, the existence and composition of the compound formed has been indicated. The compounds AuTe_2 , Bi_2Te_3 , As_2Te_3 , and many others, have thus been detected (see also p. 363). The freezing-point curves of mixtures of tellurium with sulphur⁵ and with selenium⁶ give no indication of the formation of compounds, only solid solutions being formed. The red Japanese sulphur is a solid solution containing the three elements, sulphur, selenium and tellurium.

Sodium and potassium combine with tellurium with the evolution of much heat, an atmosphere of hydrogen being advisable. The reaction may be moderated by dissolving the alkali metal in liquid ammonia; the resulting normal tellurides, Na_2Te , K_2Te , and the polytelluride, Na_4Te_3 , are easily oxidised and should be protected from the action of atmospheric oxygen.⁷ Tellurium also dissolves in fairly concentrated solutions of the alkali hydroxides, giving red solutions containing a mixture of telluride and tellurite, but if sodium hyposulphite is also present, crystalline sodium telluride can be obtained as the sole product.⁸ Fusion with potassium carbonate has a similar effect to treatment with aqueous alkali hydroxide. On the addition of water, the mixture of tellurite and telluride obtained with concentrated alkali or with fused potassium carbonate, undergoes decomposition, with liberation of tellurium.⁹

Tellurium displaces some of the nobler metals, such as gold and silver and to a less extent copper, from solutions of their salts, thus showing

¹ Moissan, *Ann. Chim. Phys.*, 1887, [vi.], 12, 521.

² Berzelius, *Pogg. Annalen*, 1833, 28, 392; 1834, 32, 1, 577; Thomsen, *Ber.*, 1882, 15, 3024.

³ Lenher, *J. Amer. Chem. Soc.*, 1908, 30, 737; MacIvor, *Chem. News*, 1902, 86, 308; von Horvath, *Zeitsch. anorg. Chem.*, 1911, 70, 408.

⁴ Prandtl and Börsch, *ibid.*, 1909, 62, 237.

⁵ Guthrie and Flury, *ibid.*, 1902, 32, 273; MacIvor, *Chem. News*, 1903, 87, 209; Pellini, *Atti R. Accad. Lincei*, 1909, [v.], 18, i., 701; Jaeger, *Proc. K. Akad. Wetensch. Amsterdam*, 1910, 12, 602; Chikashigé, *Zeitsch. anorg. Chem.*, 1911, 72, 109.

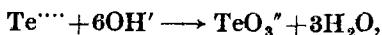
⁶ Pellini and Vio, *Atti R. Accad. Lincei*, 1906, [v.], 15, ii., 46; Kimata, *Mem. Coll. Sci. Kyōto*, 1915, 1, 119.

⁷ Tibbals, *J. Amer. Chem. Soc.*, 1909, 31, 902.

⁸ Tschugaeff and Chlopin, *Ber.*, 1914, 47, 1296; *J. Russ. Phys. Chem. Soc.*, 1915, 47, 364.

⁹ Berzelius, *Schweigger's J.*, 1822, 33, 29; Le Blanc, *Zeitsch. Elektrochem.*, 1906, 12, 649.

some resemblance to the metals,¹ but its true position as a metalloid is well seen from its behaviour in the form of electrodes in alkaline solution, when, under the influence of the current, it dissolves at both electrodes, as positive Te^{+++} ions at the anode and as negative Te^- ions at the cathode.² Both these ions are themselves colourless but have a tendency to complex formation, the negative ions dissolving tellurium to form deeply coloured polytelluride ions, Te_x^- , whilst the positive ions react with hydroxyl ions thus :



a reaction which explains the formation of tellurous acid by the action of water on tellurium tetrachloride (see p. 382). If either of the tellurium electrodes is replaced by one of platinum, finely divided tellurium separates at that electrode.³ The element can be deposited at a lead cathode in smooth, thick layers, with theoretical current efficiency, from a bath containing⁴ a solution of the following composition per litre: TeO_2 , 300 grams; HF (48 per cent.), 500 grams; H_2SO_4 , 200 grams. A current of 1.6 amps./dm.² is passed at the ordinary temperature, and with a tellurium anode containing selenium, the latter element remains entirely in the slimes, so that such a bath may be used for refining tellurium. If hydrochloric acid is used instead of hydrofluoric acid, the result is less satisfactory.

Corresponding with the increase in metallic tendency, tellurium appears to enter less readily than selenium and sulphur into the composition of organic compounds; in organic combination it can exert both bi- and quadri-valency.⁵

Physiological Action.—Tellurium compounds in solution generally possess a "metallic" taste,⁶ but the tellurites and tellurates do not exert any very poisonous action, although human beings appear more sensitive to the compounds than dogs and are easily indisposed by small quantities. A striking effect of these compounds is the persistent garlic-like odour they impart to the breath and excreta, said to be due to methyl telluride.⁷ When saliva is incubated with telluric acid and hydrazine hydrate, the colloidal tellurium formed immediately flocculates and at the same time the diastasic-like action of the saliva is destroyed.⁸ Nascent selenium produces a similar effect.

Free tellurium and insoluble tellurium compounds resist bacterial action, but the soluble tellurites and tellurates are decomposed by

¹ Senderens, *Compt. rend.*, 1887, 104, 175; Hale and Lenher, *J. Amer. Chem. Soc.*, 1902, 24, 918; Bottger, *J. prakt. Chem.*, 1874, [ii.], 9, 195.

² Le Blanc, *Zeitsch. Elektrochem.*, 1905, 11, 813; 1906, 12, 649; Muller and Nowakowski, *ibid.*, 1905, 11, 931.

³ For the electrochemical behaviour of tellurium and electrical potential measurements in various types of cells, see Euler, *Zeitsch. anorg. Chem.*, 1904, 41, 93; Reichinstein, *Zeitsch. physikal. Chem.*, 1921, 97, 257; Kasarnowsky, *Zeitsch. anorg. Chem.*, 1923, 128, 17, 33; 130, 140; Schuhmann, *J. Amer. Chem. Soc.*, 1925, 47, 356; Piccardi, *Atti R. Accad. Lincei*, 1927, [vi.], 6, 305, 428.

⁴ Mathers and Turner, *J. Amer. Electrochem. Soc.*, 1928, 54, 293.

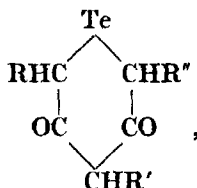
⁵ Wohler and Dean, *Annalen*, 1840, 35, 111; Mallet, *ibid.*, 1856, 97, 223; Becker, *ibid.*, 1876, 180, 263; Steiner, *Ber.*, 1901, 34, 570; Lyons and Bush, *J. Amer. Chem. Soc.*, 1908, 30, 831; Lederer, *Ber.*, 1911, 44, 2287; 1913, 46, 1358; 1914, 47, 277; *Annalen*, 1912, 391, 326; 1913, 399, 280; Morgan and others, *Trans. Chem. Soc.*, 1924, 125, 731, 754, 760, 1601; 1925, 127, 797; Drew and Thomason, *J. Chem. Soc.*, 1927, p. 116.

⁶ Hansen, *Annalen*, 1853, 86, 208. ⁷ Mead and Gies, *Amer. J. Physiol.*, 1902, 5, 104.

⁸ Labos, *Arch. exp. Pathol. Pharmacol.*, 1928, 133, 57.

micro-organism growths, with development of a dark discoloration and in some cases the characteristic garlic odour.¹ The free element in the finely divided condition, and also certain tellurium compounds, have a curative effect on the disease syphilis, although in certain cases treatment is complicated by the occurrence of undesirable reactions.²

Certain tellurium derivatives of the aliphatic β -diketones, for example, *cyclotelluropentane-3 : 5-diones* of the type



where R, R' and R'' represent hydrogen or alkyl radicals, exhibit powerful bactericidal action which, however, is greatly diminished in the presence of serum. Such compounds, which are obtained by condensation of the diketone with tellurium tetrachloride in chloroform solution, have been employed successfully in the treatment of cystitis and eye infections, and may be prepared on a pharmaceutical scale.³

Atomic Weight.—The atomic weight of tellurium is one which has been the subject of much investigation on account of the position of the element in the Periodic Table. Tellurium must on common-sense grounds be classed in Group VI along with sulphur and selenium (see Chap. I), rather than with the halogens in Group VII, in spite of the fact that if the atomic weights (I, 126.92; Te, 127.5) were alone considered tellurium would be ranked with the halogens and iodine with sulphur and selenium. Mendeléef⁴ and Brauner⁵ expressed the opinion that this apparent anomaly in the table was due to the presence in the tellurium of a small amount of an element, similar to tellurium but of higher atomic weight, and this opinion has been upheld by Bettel⁶ and by Browning and Flint.⁷ Many other investigators,⁸ however, consider tellurium to be homogeneous, and all attempts at a separation have led to negative results.

The work of Aston⁹ and others has shown that a property of an element which is more fundamental than its atomic weight is its atomic number, or the number of resultant positive charges on the nucleus of

¹ Rosenheim, *Proc. Chem. Soc.*, 1902, 18, 138; Gosio, *Atti R. Accad. Lincei*, 1904, [v.], 13, i., 422.

² Fournier, Levaditi and Guénou, *Ann. Inst. Pasteur*, 1927, 41, 443; Levaditi and others, *ibid.*, p. 369.

³ Morgan and others, *loc. cit.*; *J. Soc. Chem. Ind.*, 1924, 43, 304 T; 1925, 44, 462 T; *Biochem. J.*, 1923, 17, 30; 1924, 18, 190; Morgan and Burgess, *English Patent*, 292222 (1927). For the fungicidal action of alkali tellurites and of tellurium hydrogen tartrate, see Stover and Hopkins, *Ind. Eng. Chem.*, 1927, 19, 510.

⁴ Mendeléef, *Trans. Chem. Soc.*, 1889, 55, 649.

⁵ Brauner, *ibid.*, p. 411.

⁶ Bettel, *Chem. News*, 1908, 97, 169.

⁷ Browning and Flint, *Amer. J. Sci.*, 1909, 28, 347; Flint, *ibid.*, 1910, 30, 209; 1912, 34, 1325.

⁸ Norris, Fay and Edgerly, *Amer. Chem. J.*, 1900, 23, 105; Baker and Bennett, *Trans. Chem. Soc.*, 1907, 91, 1849; Lenher, *J. Amer. Chem. Soc.*, 1908, 30, 741; Harcourt and Baker, *Trans. Chem. Soc.*, 1911, 99, 1311; Pellini, *Atti R. Accad. Lincei*, 1912, [v.], 21, i., 218; Dudley and Jones, *J. Amer. Chem. Soc.*, 1912, 34, 995.

⁹ Aston, *Trans. Chem. Soc.*, 1921, 119, 677.

the atom. When arranged in order of atomic number, tellurium precedes iodine.

Measurements of the wave-lengths of lines in the high frequency spectra of iodine and tellurium by the primary ray method have given

$$\lambda = 0.437 \times 10^{-8} \quad \text{and} \quad \lambda = 0.388 \times 10^{-8} \text{ cm.}$$

for the wave-lengths of the α_1 and β_1 lines in the spectrum of iodine, the corresponding values for tellurium being

$$\lambda = 0.456 \times 10^{-8} \quad \text{and} \quad \lambda = 0.404 \times 10^{-8} \text{ cm.}$$

These numbers satisfy Moseley's formula connecting the frequency with the atomic number if the atomic numbers of tellurium and iodine are respectively 52 and 53.¹

The atomic weight of tellurium was determined for the first time by Berzelius in 1812, the value obtained being 129.2. The tellurium used, however, was impure, a fact only recognised in 1817.² In 1833 Berzelius repeated his determinations,³ converting tellurium into its dioxide; this time he obtained the value⁴ 128.34.

In 1858 von Hauer⁵ prepared and analysed the double bromide of potassium and tellurium, K_2TeBr_6 , and obtained the value 127.8.

Wills in 1879⁶ also adopted the preceding method and as a result of five experiments obtained the mean value 127.1. Wills also used the oxidation method of Berzelius, first using nitric acid as the oxidising agent and obtaining as the mean of five experiments the value 128.1, then using aqua regia, the mean of four experiments giving the value 128.2. With aqua regia the results were very much more consistent than with nitric acid. Many other workers have repeated these determinations at later dates, obtaining results slightly differing among themselves, but all higher than the atomic weight of iodine.

Brauner, after trying various unsatisfactory methods, prepared and analysed pure tellurium tetrabromide,⁷ obtaining the value 127.54.

A method involving the analysis of the basic nitrate, $2TeO_2.HNO_3$, which is conveniently prepared by dissolving tellurium in a slight excess of nitric acid and evaporating the solution to crystallising-point, has led to concordant results being obtained by Köthner⁸ and by Norris and his co-workers.⁹ On careful ignition of the salt the dioxide is obtained. The method was criticised by Dudley and Bowers¹⁰ as giving very irregular results, since tellurium may crystallise from nitric acid solution as tellurous acid, tellurium dioxide and basic nitrate, the exact conditions for the separation of any one of these appearing to be very elusive. Good results have been obtained, however, by Stähler and Tesch,¹¹ who first very carefully purified the tellurium used by fractional

¹ Siegbahn, *Ber. Deut. physikal. Ges.*, 1916, 18, 39.

² Berzelius, *Schweigger's J.*, 1812, 6, 311; 1818, 22, 74.

³ Berzelius, *Pogg. Annalen*, 1833, 28, 395; 1834, 32, 14.

⁴ The results given are from calculations based on the following fundamental values: O=16.000; Cl=35.457; Br=79.916; K=39.096; Ag=107.880.

⁵ von Hauer, *J. prakt. Chem.*, 1858, 73, 98.

⁶ Wills, *Trans. Chem. Soc.*, 1879, 37, 704.

⁷ Brauner, *ibid.*, 1889, 55, 382.

⁸ Köthner, *Annalen*, 1901, 319, 1.

⁹ Norris and Fay, *Amer. Chem. J.*, 1898, 20, 278; Norris, Fay and Edgerly, *ibid.*, 1900, 23, 105; Norris, *J. Amer. Chem. Soc.*, 1906, 28, 1675.

¹⁰ Dudley and Bowers, *ibid.*, 1913, 35, 875.

¹¹ Stähler and Tesch, *Zeitsch. anorg. Chem.*, 1916, 98, 1.

SULPHUR, SELENIUM, AND TELLURIUM.

distillation, which removes most impurities except antimony; the latter was removed by conversion to tellurium tetrachloride and fractional distillation in a stream of chlorine. The tetrachloride, dissolved in hydrochloric acid and precipitated by sulphur dioxide, yielded an amorphous product which on further distillation gave tellurium spectroscopically free from impurities. This was converted into the basic nitrate by dissolving in nitric acid and heating in a stream of dry air. On decomposition of the product by heat, tellurium dioxide was obtained, which on analysis gave the value 127.513 ± 0.003 for the atomic weight of the element.

Dudley and Bowers,¹ having first obtained pure tellurium by fractional precipitation with hydrazine hydrochloride,² synthesised the tetrabromide and obtained a mean value of 127.479 for the atomic weight.

Gutbier and Wagenknecht in 1905 carried out a series of determinations based on the reduction of tellurium dioxide to the metal.³ The reduction was effected by two distinct methods, but the results in both cases were practically the same. In the first series of experiments the dioxide was mixed with silver and powdered quartz and reduced in a current of hydrogen. In the second series the reduction was effected by means of hydrazine hydrochloride. The mean value for the atomic weight from both series of determinations was 127.62.

Marckwald, after a research with unsatisfactory material,⁴ prepared some pure tellurium dioxide from telluric acid which had been crystallised several hundred times.⁵ The dioxide was analysed volumetrically by oxidising to telluric acid by means of potassium permanganate, excess of the latter being determined by means of oxalic acid. The mean result obtained was 127.61.

Lenher⁶ determined the atomic weight of tellurium by decomposing weighed amounts of potassium telluribromide, K_2TeBr_6 , by means of chlorine and hydrogen chloride, and weighing the potassium chloride which remained. Using tellurium ores from three different sources, the oxide obtained was converted into the double bromide by the action of hydrobromic acid and potassium bromide; the telluribromide formed was crystallised repeatedly from water. As a mean of sixteen concordant experiments Lenher obtained the value 127.55.

The apparent simplicity of the foregoing method and the close agreement of the results obtained led Dennis and Anderson⁷ to employ it in their investigations. These workers found, however, that it was impossible to free the potassium telluribromide from water without causing partial decomposition of the salt. They then prepared hydrogen telluride by electrolysis and oxidised it by passing it into nitric acid, calculating the atomic weight of tellurium from titration of the resulting dioxide with potassium permanganate. The average result was 127.50.

The method of Bruylants and Desmet⁸ was similar to the foregoing. Tellurium prepared from hydrogen telluride was treated with nitric acid and the resulting dioxide separated by evaporation, calcined, and

¹ Dudley and Bowers, *loc. cit.* See also Baker and Bennett, *Trans. Chem. Soc.*, 1907, 91, 1849. ² See Dudley and Jones, *J. Amer. Chem. Soc.*, 1912, 34, 995.

³ Gutbier and Wagenknecht, *Annalen*, 1905, 342, 266.

⁴ Marckwald, *Ber.*, 1907, 40, 4730; Baker, *Chem. News*, 1908, 97, 209.

⁵ Marckwald and Foisik, *Ber.*, 1910, 43, 1710.

⁶ Lenher, *J. Amer. Chem. Soc.*, 1908, 31, 20.

⁷ Dennis and Anderson, *ibid.*, 1914, 36, 882.

⁸ Bruylants and Desmet, *Bull. Soc. chim. Belg.*, 1914, 28, 264.

dissolved in aqueous sodium hydroxide. The tellurium was then estimated volumetrically either in alkaline¹ or just acid² solution. The mean of twelve estimations in alkaline solution gave the value 127·8, and of nine estimations in acid solution the value 127·65.

Hydrogen telluride was also the starting-point in the investigation of Bruylants and Michielsen.³ The gas after careful purification was decomposed into its elements at 200° to 220° C., the tellurium weighed as such and the hydrogen oxidised to water by means of cupric oxide. The value obtained was 127·8.

Baker and Bennett⁴ adopted a method apparently not used by any other investigator, but which is applicable to elements which lie on the border line between metals and non-metals. Tellurium dioxide was reduced to the element by heating with sulphur in a current of nitrogen, the sulphur being oxidised to sulphur dioxide. From the ratio $\text{TeO}_2 : \text{SO}_2$, the value obtained for the atomic weight was 127·609. This result, however, is high, and it was found that some sulphur trioxide was also formed.

The value adopted by the Chemical Society on the recommendation of the Sub-Committee on Atomic Weights (1929) is $\text{Te} = 127·5$.

Tellurium is a mixture of three isotopes,⁵ the mass-numbers of which are 128, 130 and 126. The intensities of the first two are about equal and double that of the third, so that it would seem probable that the mean atomic weight is at least as high as 128. The discrepancy between this conclusion and the actual values obtained remains to be explained. Tellurium is unique in that *all* its mass-numbers form members of isobaric pairs, these being shared by xenon, the element of next higher even atomic number. The atomic number of tellurium is 52.

Alloys.—As has already been mentioned, tellurium combines with many metals giving compounds the existence of which has usually been demonstrated by investigation of the freezing-point curves of mixtures in varying proportions. In this way the combinations, TeCd (1041° C.), TeSn (780° C.), Te_2Au , TeZn (1238° C.), TeHg , Te_3As_2 , Te_3Bi_2 , Te_3Sb_2 , TeCu_2 , Te_3Cu_4 , TeSn (769° C.), etc., have been detected, the bracketed figures giving the corresponding melting-points. The alloys are of no practical importance except in so far as they occur in nature and serve as sources of the respective constituents.⁶

¹ See Brauner, *Trans. Chem. Soc.*, 1891, 59, 250.

² See Gooch and Howland, *Zeitsch. anorg. Chem.*, 1894, 7, 132.

³ Bruylants and Michielsen, *Bull. Acad. roy. Belg.*, 1919, [v], 5, 119.

⁴ Baker and Bennett, *Trans. Chem. Soc.*, 1907, 91, 1849.

⁵ Aston, *Nature*, 1924, 114, 717; *Phil. Mag.*, 1925, [vi], 49, 1196.

⁶ For a bibliography of these alloys up to 1903, see Sack, *Zeitsch. anorg. Chem.*, 1903, 53, 249. Later investigations have been made by Heyn and Bauer, *Metallurgie*, 1906, 3, 273 (Cu—Te); Pélabon, *Compt. rend.*, 1906, 142, 1147 (Sn—Te); p. 207 (Sb—Te); 1907, 145, 118 (Ti—Te); 1908, 146, 1397 (As—Te, Bi—Te); 1909, 148, 1176 (Au—Te); Fay, *J. Amer. Chem. Soc.*, 1907, 29, 1265 (Sn—Te); Chikashigé, *Zeitsch. anorg. Chem.*, 1907, 54, 50; Pellini, *Atti R. Accad. Lincei*, 1909, [v], 18, n., 211 (Hg—Te); *Gazzetta*, 1915, 45, i., 469 (Au—Te—Ag); Biltz and Mecklenburg, *Zeitsch. anorg. Chem.*, 1909, 64, 226 (Sn—Te); Tibbals, *J. Amer. Chem. Soc.*, 1909, 31, 902 (various); Kobayashi, *Zeitsch. anorg. Chem.*, 1910, 69, 1 (Cd—Te, Sn—Te); *Mem. Coll. Sci. Eng. Kyōto*, 1911, 3, 217 (Zn—Te); Coste, *Compt. rend.*, 1911, 152, 859 (Au—Te); Kimura, *Mem. Coll. Sci. Kyōto*, 1915, 8, 149 (Pb—Te); Kimata, *ibid.*, 1915, 1, 115 (Sb—Te); p. 119 (Se—Te); Chikashigé and Saito, *ibid.*, 1916, 1, 361 (Ag—Te); Chikashigé and Nosé, *ibid.*, 1917, 2, 227 (Al—Te); Saldau, *Jahrb. Miner.*, 1915, ii., Ref. 21 (Pb—Te); Dreifuss, *Zeitsch. Elektrochem.*, 1922, 28, 100, 224 (Sb—Pb—Te); Sisoo and Whitmore, *Ind. Eng. Chem.*, 1924, 16, 838 (Al—Cu—Te); Endo, *Sci. Rep. Tōhoku Imp. Univ.*, 1927, 16, 201 (Pb, Sn, Sb, Bi—Te).

The Detection and Estimation of Tellurium.

Detection.—Dry Tests.—When heated on charcoal in a reducing flame tellurium compounds give rise to free tellurium, which volatilises and forms a crust of the dioxide around the heated area; the flame also is tinged with green. There is no marked odour. In the hydrogen-air flame, tellurium dioxide, hydrogen telluride and elementary tellurium all produce a lilac luminescence in the middle zone and a green luminescence in the outer zone. In the inner zone hydrogen telluride produces blue luminescence, while the colour imparted by the other two compounds is green in this region. The vapour of tellurium dioxide introduced into a Bunsen flame produces a blue coloration tinged with green. If a cold surface is held in the hottest part of the flame a bright metallic mirror is deposited on it.¹ The green luminescence appears to be due to the change from tellurium to tellurous salt, and the blue to the further oxidation to telluric salt.²

Wet Tests.—A test for tellurium which is sensitive to 10 mgms. per litre, consists in boiling 1 c.c. of solution with 1 c.c. of concentrated ammonia and a few crystals of hydrazine sulphate. If tellurium is present a brown coloration or precipitate appears. If selenium is present, it is first removed by boiling the solution with an equal bulk of concentrated sulphuric acid and a few crystals of hydrazine sulphate; the precipitate is removed and the filtrate made alkaline with ammonia, more hydrazine sulphate added and the solution again boiled; a brown coloration indicates the presence of tellurium.³

Another method⁴ for the detection of tellurium in the presence of selenium depends on the fact that the former is not precipitated by sulphur dioxide in the presence of concentrated hydrochloric acid. A solution in the concentrated acid (dens. 1.16) is heated to 90° C. and saturated with sulphur dioxide; the precipitated selenium is removed by filtration, the filtrate diluted with an equal volume of water and saturated in the cold with sulphur dioxide. If tellurium is present a black precipitate is formed immediately.

Tellurites and tellurates may be reduced to tellurium by means of titanous chloride in hydrochloric acid solution, and in the absence of selenium, copper, gold and platinum, the reaction may be used as a sensitive test for the element.⁵ In 5 c.c. of concentrated hydrochloric acid, 0.00005 gram of tellurium gives with 2 c.c. of a 2 per cent. titanous chloride solution a grey cloud which slowly flocculates. In the presence of a little acetic acid and a large quantity of sodium acetate, reduction to hydrogen telluride results; this gas may be detected by its disagreeable odour and by the production of a mirror on passing it through a heated tube.

A microchemical test, in which the tellurium is precipitated by means of a saturated solution of quinol in concentrated sulphuric acid, has been described.⁶ The quinol reagent, however, also reacts with selenium and manganese.⁷

¹ Papish, *J. Physical Chem.*, 1918, 22, 430, 640.

² See Weiser and Garrison, *ibid.*, 1919, 23, 478.

³ Müller, *Zeitsch. physikal. Chem.*, 1922, 100, 346.

⁴ Dennis and Koller, *J. Amer. Chem. Soc.*, 1919, 41, 949.

⁵ Tomiček, *Bull. Soc. chim.*, 1927, [iv.], 41, 1399.

⁶ Putnam, Roberts and Selchow, *Amer. J. Sci.*, 1928, [v.], 15, 253.

⁷ For a colour reaction with potassium cyanide, see Hinrichsen and Bauer, *Metallurgie*, 1907, 4, 315.

Estimation.—Gravimetric.—Tellurium is generally precipitated as the element and weighed as such. It may be liberated from its compounds by various reducing agents such as sulphurous acid and its salts (sometimes with the addition of an iodide), hypophosphorous acid, hydrazine salts, glucose,¹ or by electrolysis. The precipitate should be washed with alcohol and dried at 110° C. At this temperature oxidation of the element is extremely slight, but if the utmost accuracy is required the drying should be carried out in an atmosphere of nitrogen.

The use of sulphur dioxide as precipitant was first proposed by Berzelius, but accurate results by this method are only obtainable under special conditions. Complete precipitation does not take place from a strongly acid solution, and in the presence of other metals small amounts of these are liable to be carried down. In the presence of heavy metals such as copper, bismuth and antimony, the following procedure has been recommended:² The tellurium is oxidised to telluric acid by the addition of ammonium perdisulphate in the presence of potassium hydroxide, excess of perdisulphate being subsequently removed by boiling. The heavy metals present are next removed by means of hydrogen sulphide. The tellurium may then readily be estimated by reduction with hydrogen chloride and precipitation with sulphurous acid.

Tellurous acid is rapidly reduced to the element by sulphurous acid in the presence of potassium iodide.³ Owing, however, to the affinity which tellurium has for iodine and the consequent formation of varying proportions of tellurium tetra-iodide, the trustworthiness of the quantitative method based on this reaction is questionable.⁴

Solutions of tellurium in alkali sulphides when boiled with sodium sulphite yield a quantitative precipitate of the element.⁵

An aqueous solution of telluric acid gives with hypophosphorous acid a colloidal solution of tellurium which is precipitated completely on boiling and can then be filtered and weighed. This method is only available if there are no other salts present which might be reduced.⁶

Tellurium in the sexavalent condition cannot be estimated using phosphorous acid as reducing agent since complete reduction does not take place. Tellurium in the tellurous condition is reduced readily to the elementary condition when its concentrated solution in hydrochloric acid is boiled with phosphorous acid.⁷

Of the various methods of estimation which are based on the use of hydrazine salts as reducing agents the following appears to be one of the most satisfactory:⁸ The tellurium, present either as a derivative of the dioxide or as a tellurate, is dissolved in hydrochloric acid and boiled. Sulphurous acid and hydrazine hydrochloride are added, and on continued boiling the tellurium is precipitated as such and may be collected,

¹ For methods of estimation using glucose as reducing agent, see Kolbe, *Zeitsch. anal. Chem.*, 1872, 11, 437; Kastner, *ibid.*, 1875, 14, 142; Donath, *Zeitsch. angew. Chem.*, 1890, 4, 214.

² Brauner and Kuzma, *Ber.*, 1907, 40, 3362.

³ Frerichs, *J. prakt. Chem.*, 1902, [ii.], 66, 261; MacIvor, *Chem. News*, 1903, 87, 17.

⁴ See Gutbier and Wagenknecht, *J. prakt. Chem.*, 1905, [ii.], 71, 54; Gutbier and Flury, *Chem. News*, 1909, 99, 217.

⁵ For the use of this reaction in the separation of tellurium from the heavy metals and selenium, see Brukl and Maxymowicz, *Zeitsch. anal. Chem.*, 1926, 68, 14.

⁶ Gutbier, *Zeitsch. anorg. Chem.*, 1902, 32, 295.

⁷ Gutbier, *ibid.*, 1904, 41, 448.

⁸ Lenher and Homberger, *J. Amer. Chem. Soc.*, 1908, 30, 387; Gutbier and Huber, *Zeitsch. anal. Chem.*, 1914, 53, 430.

dried and weighed.¹ If selenium is present it may be separated first by passing sulphur dioxide into the solution in concentrated hydrochloric acid.²

Electrolytic Methods.—According to Müller's experiments,³ tellurium is not deposited by electrolysis from solutions in which it is present in the sexavalent condition, so that telluric acid must first be reduced to tellurous acid. A weight of tellurous acid not exceeding 0.25 gram is dissolved in 175 c.c. of 2N H_2SO_4 and electrolysed for two and a half hours between platinum electrodes. The grey deposit of tellurium is washed with water and alcohol and dried in a desiccator over sulphuric acid. In this method the average error is estimated to be ± 0.1 per cent. By this process tellurous acid may be estimated in the presence of telluric acid. After the tellurium from the tellurous acid has been removed, the solution is boiled with hydrochloric acid to reduce the telluric acid to tellurous acid and the estimation of the tellurium carried out as before.⁴

A method for the estimation of tellurium in *tetradymite* (p. 350) is given by Hulot.⁵ The mineral is first treated with dilute hydrochloric acid to remove calcareous material. The residue is powdered and dissolved in hot concentrated nitric acid. After evaporation of the solution the solid is fused with potassium nitrate, the resulting mass containing potassium sulphate and selenate, bismuth oxide and potassium anhydrotellurate, $\text{K}_2\text{Te}_4\text{O}_{13}$. The sulphate and selenate are removed by digestion with boiling water and the bismuth oxide is dissolved out with dilute hydrochloric acid. The residue, potassium anhydrotellurate, is suspended in dilute hydrochloric acid and zinc added. A black pulverulent powder is deposited, which is pure tellurium. After the whole of the zinc has dissolved, the tellurium may be collected, dried and weighed.

In the processes described in which the tellurium is precipitated in the elementary form, it is generally assumed (see p. 365) that the error due to oxidation of the precipitate is practically negligible under the conditions of the experiment. Browning and Flint,⁶ however, maintain that the results are liable to be inaccurate owing to this oxidation. Tellurium dioxide, on the other hand, is unaffected by the air, is anhydrous, non-hygroscopic and easily obtained in the pure condition, and Browning and Flint base a method for the estimation of tellurium on precipitation as dioxide. The tellurium compound is precipitated from a faintly acid solution by means of ammonia, the acidity being restored by the cautious addition of acetic acid. The mixture is heated for some time to render the precipitate crystalline. The method is applicable to the separation of tellurium from selenium.⁷

¹ See also Gutbier, *Chem. Zentr.*, 1904, ii., 1554; Gutbier and Rosenscheck, *Zeitsch. anorg. Chem.*, 1902, 32, 260; Rosenheim and Weinheber, *ibid.*, 1911, 69, 266; Pellini, *Gazzetta*, 1903, 33, i., 515.

² Lenher and Kao, *J. Amer. Chem. Soc.*, 1925, 47, 769, 2454; Lenher and Smith, *Ind. Eng. Chem.*, 1924, 16, 837.

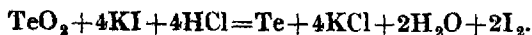
³ Müller, *Zeitsch. physikal. Chem.*, 1922, 100, 346.

⁴ For other methods of electrolytic estimation of tellurium, see Pellini, *Atti R. Accad. Lincei*, 1903, [v.], 12, ii., 312; 1904, 13, [ii.], 275; Gallo, *ibid.*, 1904, [v.], 13, i., 713; 14, i., 23, 104; Lukas and Jilek, *Chem. Listy*, 1926, 20, 396; *Brit. Chem. Abs.*, 1926, A, 1018.

⁵ Hulot, *Bull. Soc. chim.*, 1920, [iv.], 27, 100.
⁶ Browning and Flint, *Amer. J. Sci.*, 1909, [iv.], 28, 112; *Zeitsch. anorg. Chem.*, 1909, 64, 104.

⁷ See also Berg, *Bull. Soc. chim.*, 1905, [iii.], 33, 1310.

According to Perkins¹ electrolytic silver may be used in the quantitative estimation of tellurium. Tellurium dioxide, like selenium dioxide, liberates iodine from an acidified solution of potassium iodide according to the equation:



The liberated iodine may be estimated by shaking with specially prepared electrolytic silver in an atmosphere of hydrogen and measuring the increase in weight of the silver. The increase in weight represents the iodine liberated plus the tellurium (or selenium).

Volumetric Estimation.—Tellurium may be determined by oxidation from the tellurous to the telluric condition, using an excess of potassium dichromate or permanganate and subsequently titrating the excess of oxidising agent with a standard solution of a suitable reducing agent.² In order to obtain accurate results with the potassium dichromate titration, certain very definite steps in the procedure are essential, and it is necessary to control the course of the reaction, since hydrochloric and telluric acids interact with production of chlorine.



The following procedure³ has been found very satisfactory. The hydrochloric acid solution of the dioxide is treated with an excess of standard dichromate and allowed to react for at least half an hour. A measured excess of ferrous ammonium sulphate is added and the excess of ferrous salt titrated with standard dichromate, using potassium ferricyanide as outside indicator. The weight of tellurium dioxide should be less than 0.3 gram, and the solution, the volume of which should be approximately 200 c.c., should contain 2 per cent. of free hydrogen chloride for successful working.⁴

Tellurous acid cannot be determined by oxidation with potassium permanganate in acidified solution, but in alkaline solution accurate results may be obtained by cooling to 8°–10° C. after the oxidation and slowly acidifying with dilute sulphuric acid, with continual stirring. Excess of standard oxalic acid is then added and after warming to 50° C. the remaining excess is titrated with permanganate.⁵

Telluric acid may be determined iodometrically by reduction with either hydrogen bromide or hydrogen chloride.⁶ The substance⁶ is heated in a distillation flask with four times the theoretical quantity of potassium iodide in the presence of the acid, air being excluded from the apparatus by passing a stream of carbon dioxide. The liberated iodine is titrated in the receiver and in the residue.⁷

¹ Perkins, *Amer. J. Sci.*, 1910, [iv.], 29, 540.

² Brauner, *Monatsh.*, 1892, 12, 34; Gooch and Peters, *Amer. J. Sci.*, 1899, [iv.], 2, 271.

³ Lenher and Wakefield, *J. Amer. Chem. Soc.*, 1923, 45, 1423. See also Moser and Miksch, *Monatsh.*, 1924, 44, 349, for a method involving oxidation in neutral solution.

⁴ For a modification of this method in which the end-point is determined electro-metrically, see Schrenk and Browning, *J. Amer. Chem. Soc.*, 1926, 48, 139.

⁵ Moser and Miksch, *loc. cit.* See also Brauner, *Trans. Chem. Soc.*, 1891, 59, 250. For a method in which the excess of permanganate is determined iodometrically in the presence of sodium acetate, see Norris and Fay, *Amer. Chem. J.*, 1898, 20, 278.

⁶ Moser and Prinz, *Zeitsch. anal. Chem.*, 1918, 57, 277; Moser and Miksch, *loc. cit.*

⁷ Cf. Gutbier and Resenschek, *Chem. Zentr.*, 1904, ii., 1555. See also Menke, *Zeitsch. anorg. Chem.*, 1912, 77, 282.

Other methods have been described which depend on reduction of the tellurium compound by means of titanous chloride, but these generally are not trustworthy owing to the formation of hydrogen telluride. Potentiometric titration with titanous chloride in the presence of hydrochloric acid has been recommended.¹

Telluric acid may also be estimated alkalimetrically² by the addition of a large excess of standard barium hydroxide, or sodium hydroxide containing barium chloride, when barium tellurate is quantitatively precipitated. The excess of the hydroxide is determined by titration with oxalic acid, phenolphthalein being used as indicator.

¹ Tomiček, *Bull. Soc. chim.*, 1927, [iv.], 41, 1389.

² Rosenheim and Weinheber, *Zeitsch. anorg. Chem.*, 1911, 69, 266.

CHAPTER VII.

COMPOUNDS OF TELLURIUM.

IN its chemical behaviour tellurium shows considerable resemblance to sulphur and selenium, and its inclusion in the same group with these elements was due in the first place to the analogy in the composition of many of its compounds with that of compounds of sulphur and selenium. There are, however, important characteristics which differentiate the compounds of tellurium from those of the other elements of the group. Like sulphur and selenium, the element exhibits bi-, quadri- and sexavalency, but those compounds containing tellurium in the quadrivalent condition are the most stable. Moreover, in this condition tellurium appears to resemble platinum somewhat, there being evidence that the four valencies are directed symmetrically about the atom in a simple square configuration, possibly in one plane (*cf.* the spatial arrangement of the sulphur atom, p. 40); thus compounds such as dimethyltellurium dihalides, TeMe_2X_2 ($\text{X}=\text{Cl}, \text{Br}$ or I), are known to exist in two distinct isomeric forms, α - (*trans*-) and β - (*cis*-) forms,¹ although it must be mentioned that the molecular structure of these compounds is a matter of controversy, and conductivity measurements show that in aqueous solution one of the halogen atoms is hydrolysed more or less completely, whilst the other atom forms a halogen ion,² for example :



The basic tendencies of tellurium also lead to important characteristic differences in the properties of its compounds compared with the properties of its sulphur and selenium analogues.

Tellurium forms only one compound with hydrogen, hydrogen telluride, H_2Te , which is a gas at ordinary temperatures and resembles hydrogen sulphide in its ability to precipitate as tellurides many heavy metals from their solutions, although the conditions of such precipitation do not appear to have been fully investigated. As already described, many of the tellurides occur in nature. With each of the halogens tellurium forms a tetrahalide of the type TeX_4 , which with water produces tellurous acid. The tetrahalides show a marked tendency to form additive compounds, and except in the case of the fluoride, yield with alkali halides co-ordinative compounds of the type R_2TeX_6 , analogous with the platinum compounds. The only other halides known are the hexafluoride, TeF_6 , the dichloride, TeCl_2 , and the dibromide, TeBr_2 , the last two being very unstable under ordinary conditions of temperature and pressure. Certain indefinite oxyhalides have also been isolated.

Oxides of composition TeO , TeO_2 and TeO_3 are known, as well as a fourth compound, Te_3O_7 , which appears to be a basic tellurium tellurate,

¹ Vernon, *Trans. Chem. Soc.*, 1920, 117, 86, 889; 1921, 119, 105, 687.

² Lowry, Goldstein and Gilbert, *J. Chem. Soc.*, 1928, p. 307.

TeO_2 , TeO_3 (see p. 387). The dioxide is only slightly soluble in water and the aqueous solution does not redden litmus; it dissolves in aqueous alkalis with formation of tellurites, from solutions of which tellurous acid, H_2TeO_3 , may be precipitated (see p. 382). This compound is also only slightly soluble in water, but its solution is sufficiently acid to redden litmus. The acid is very unstable and readily loses water to form the dioxide; this tendency to dehydration is characteristic of acids derived from elements with weak metallic properties, the oxides of which are feeble anhydrides. That the dioxide also has definite basic properties is shown by its reaction with many acids to produce salt-like compounds containing quadrivalent tellurium, as, for example, the tetrahalides and the sulphates (p. 381). Tellurium trioxide, obtained by heating telluric acid, is unacted on by water, and is readily reduced to the dioxide. Telluric acid, which is produced by the action of powerful oxidising agents on tellurium, is a very weak acid, but it is a more effective oxidising agent than sulphuric acid and, like selenic acid, is able to liberate chlorine from hydrochloric acid. Telluric acid shows a greater tendency than its sulphur and selenium analogues to enter into the formation of complex compounds such as heteropoly-acids (see p. 388).

The few compounds of tellurium with the elements sulphur, carbon and nitrogen which have been investigated, are described later (pp. 388-391). Most tellurium compounds are colourless, but the sulphur compounds, as well as the polytellurides, are in general dark red. A similar deepening of colour occurs in the polysulphides and polyselenides.

TELLURIUM AND HYDROGEN.

Hydrogen Telluride, H_2Te .—In 1808 the observation was made by Ritter¹ that in the electrolysis of water using a tellurium cathode, an unstable tellurium-hydrogen compound was produced, and in repeating this experiment with potassium hydroxide solution as electrolyte, Sir Humphry Davy two years later further observed the formation of a deep red solution. Berthelot and Fabre in 1887 first prepared the hydrogen compound in a state approaching purity.²

Preparation.—(1) Tellurium can be reduced to hydrogen telluride by strongly heating in an atmosphere of hydrogen (see p. 357), but the yield is very poor, and the purer the tellurium the greater is the resistance against the action of hydrogen.³ The reduction can also be effected by zinc and dilute sulphuric acid, the tellurium being conveniently added as the dioxide,⁴ but the most satisfactory method of reduction is to make tellurium the cathode in an electrolysis, at 0°C . or lower, of 50 per cent. sulphuric acid or preferably phosphoric acid; the evolved gas may contain 5 to 10 per cent. of free hydrogen.⁵

(2) Hydrogen telluride is also obtainable from the metallic tellurides, for example, from magnesium, aluminium, zinc and iron tellurides. These are decomposed by water or by a non-oxidising acid such as dilute

¹ Ritter, *Gilbert's Annalen*, 1808, 29, 148.

² Berthelot and Fabre, *Ann. Phys. Chem.*, 1887, [vi.], 14, 103.

³ Gutbier, *Zeitsch. anorg. Chem.*, 1902, 32, 31; Hempel and Weber, *ibid.*, 1912, 77, 48.

⁴ Divers and Shimosé, *Ber.*, 1883, 16, 1014.

⁵ Poggendorff, *Pogg. Annalen*, 1848, [ii], 75, 350; Ernyei, *Zeitsch. anorg. Chem.*, 1900, 25, 313; Hempel and Weber, *ibid.*, 1912, 77, 48; Dennis and Anderson, *J. Amer. Chem. Soc.*, 1914, 36, 882.

hydrochloric or phosphoric acid. It is necessary to displace the air from the apparatus previously by means of a current of nitrogen and to collect over mercury. The hydrogen telluride may be purified by passing it through a freezing mixture of ether and solid carbon dioxide. Aluminium telluride is the most suitable telluride to use and hydrogen chloride the best acid. Under the most favourable conditions a yield of more than 80 per cent. of the theoretical may be obtained.¹

Properties.—Hydrogen telluride is a colourless gas, the odour of which is notably different from that of its selenium and sulphur analogues, being less pronounced and faintly recalling that of arseniuretted hydrogen. The gas is poisonous; a bubble inhaled is sufficient to cause a severe attack of vertigo.² The gas can be solidified to a colourless crystalline mass which at -57°C . melts to a very pale yellow liquid of boiling-point -1.8°C . at 760 mm.³ and density 2.57 at -20°C .⁴ The critical temperature lies in the region of 200°C . When freshly distilled, liquid hydrogen telluride is almost colourless, but darkens gradually on keeping, owing to the formation of tellurium, which remains dissolved in the liquid. This decomposition is greatly accelerated by daylight and by ultra-violet light.⁵

Conductivity measurements in *N*/10 aqueous solution show the dissolved gas to be ionised to the extent of 50 per cent., whilst hydrogen selenide in *N*/10 solution is only 4.1 per cent. ionised. The acidity of the hydrides of the elements oxygen, sulphur, selenium and tellurium therefore falls into the regular series $\text{H}_2\text{Te} > \text{H}_2\text{Se} > \text{H}_2\text{S} > \text{H}_2\text{O}$, in inverse order to the stability.⁶

The gas is fairly soluble in water and also in ether, the latter solvent giving a relatively stable solution.⁷ The vapour density accords very closely with that expected from the formula H_2Te .⁸

Hydrogen telluride is an unstable gas. It is an endothermic compound, the heat of formation being as follows :⁹



When the gas is kept in sealed tubes a deposit of tellurium gradually forms on the walls. This dissociation does not appear to be accelerated by light, as is the case with liquid hydrogen telluride (see before), since it occurs just as rapidly in the dark.¹⁰

Hydrogen telluride burns in air with a blue flame, producing water and tellurium dioxide. Moist air decomposes the gas immediately even at the ordinary temperature with liberation of black tellurium. The dry gas is immediately oxidised by oxygen.

Solutions of the alkalis dissolve the gas with formation of the corresponding telluride, but on account of the presence of more or less free

¹ Moser and Ertl, *Zeitsch. anorg. Chem.*, 1921, 118, 269. See also Dennis and Anderson, *J. Amer. Chem. Soc.*, 1914, 36, 882; Wöhler, *Ann. Phys. Chem.*, 1827, [ii.], 11, 161.

² Baker and Bennett, *Trans. Chem. Soc.*, 1907, 91, 1849.

³ Bruylants, *Bull. Acad. roy. Belg.*, 1920, [v.], 6, 472.

⁴ de Forcrand and Fonzes-Diacon, *Ann. Chim. Phys.*, 1902, 26, [7], 258.

⁵ Moser and Ertl, *Zeitsch. anorg. Chem.*, 1921, 118, 269.

⁶ Bruner, *Zeitsch. Elektrochem.*, 1913, 19, 861; de Hlasko, *Bull. acad. Polonaise Sci. Lettres*, 1919, A, 73.

⁷ Whitehead, *J. Amer. Chem. Soc.*, 1895, 17, 849.

⁸ Ernyei, *Zeitsch. anorg. Chem.*, 1900, 25, 313.

⁹ Berthelot and Fabre, *Ann. Phys. Chem.*, 1887, [vi.], 14, 103.

¹⁰ Dennis and Anderson, *J. Amer. Chem. Soc.*, 1914, 36, 882; Moser and Ertl, *loc. cit.*

oxygen, some free tellurium is formed and dissolves in the telluride solution, so that the solution is generally deep red in colour. If oxygen is entirely excluded the solution is colourless.¹ The solution of alkali telluride can be used for the precipitation of some of the heavier metals. Hydrogen telluride itself also precipitates many of the heavy metals as tellurides.

Hydrogen telluride is very sensitive towards the halogen elements. It not only readily reduces chlorine, bromine and iodine to the corresponding hydric acids with simultaneous liberation of tellurium (which in the case of chlorine can further pass easily into the tetrachloride), but it also reduces solutions of such salts as ferric chloride and mercuric chloride to the lower chlorides, tellurium being precipitated. It also reduces tellurium chlorides, the only products being hydrogen chloride and tellurium.

The composition of the gas is demonstrated by the action of heated tin, when the volume of hydrogen obtained is equal to that of the original gas.

Organic tellurides are known and clearly show the tendency of tellurium to pass from the bivalent condition to one of higher valency; ² thus the dialkyl tellurides act in an unsaturated manner and readily form dihalides, oxides and hydroxides, for example, $(C_2H_5)_2TeCl_2$, $(CH_3)_2TeO$.

TELLURIUM AND FLUORINE.

Two tellurium fluorides have been described, having the compositions TeF_4 and TeF_6 , respectively.

Tellurium Tetrafluoride, TeF_4 , is formed by the action of fluorine on tellurium, the heat of the reaction causing the mass to become incandescent.³

By dissolving tellurium dioxide in hydrofluoric acid and concentrating the solution, a tellurium oxyfluoride separates, which, according to Berzelius, yields on heating first water and then a sublimate of the tetrafluoride. Metzner,⁴ by cooling the solution to about $-50^\circ C.$, obtained crystals to which he assigned the formula $TeF_4 \cdot TeO_2 \cdot 2H_2O$, and on treating the mother-liquor with anhydrous hydrofluoric acid and cooling to $-70^\circ C.$, it solidified. On allowing the temperature to rise once more, the portion which remained unfused at $-28^\circ C.$ was regarded as tellurium tetrafluoride. Prideaux and Millott, however, using anhydrous hydrogen fluoride throughout, have not been able to obtain the tetrafluoride by such means.⁵ These investigators obtained a liquid which, in a vacuum desiccator, yielded a mass of white crystals of composition $TeF_4 \cdot TeO_2 \cdot H_2O$ (see later).

Tellurium tetrafluoride is a deliquescent solid which is decomposed

¹ Ernyei, *Zestach. anorg. Chem.*, 1900, 25, 313.

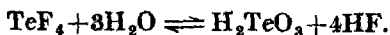
² Lyons and Bush, *J. Amer. Chem. Soc.*, 1908, 30, 831; Lederer, *Compt. rend.*, 1910, 151, 611; Ber., 1911, 44, 2287; *Annalen*, 1912, 391, 326; Vernon, *Trans. Chem. Soc.*, 1920, 117, 86, 889; 1921, 119, 105, 687; Goddard, Ashley and Evans, *ibid.*, 1922, 121, 978; Natta, *Atti II. Cong. Naz. Chim. Pura Appl.*, 1926, p. 1326; *Chem. Zentr.*, 1928, i., 2245; Gilbert and Lowry, *J. Chem. Soc.*, 1928, p. 3179; *Nature*, 1929, 123, 85; Drew, *J. Chem. Soc.*, 1929, p. 560.

³ Moissan, *Ann. Chim. Phys.*, 1891, [6], 24, 239.

⁴ Metzner, *ibid.*, 1898, [vii.], 15, 203; *Compt. rend.*, 1897, 125, 23.

⁵ Prideaux and Millott, *J. Chem. Soc.*, 1926, pp. 173, 520.

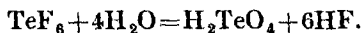
by water, forming tellurous acid. The foregoing method of preparation is therefore dependent on the reversibility of the reaction



The presence of tellurite makes a special method necessary for the estimation of the fluoride, and it is found¹ that after hydrolysis the hydrogen fluoride may be titrated with alkali, using *p*-nitrophenol as indicator, the end-point not being affected by the presence of tellurous acid.

Tellurium tetrafluoride combines with the fluorides of the alkali metals (including ammonium) and barium fluoride, producing colourless crystalline salts of the general formula $\text{XF} \cdot \text{TeF}_4$, in which X represents the equivalent weight of the metal.²

Tellurium Hexafluoride, TeF_6 , appears to be more stable than tellurium tetrafluoride. It has been obtained by the action of fluorine on tellurium at -78°C .³ The resulting colourless crystalline solid vaporises on allowing the temperature to rise. The solidified substance melts at -86°C . and boils at -35.5°C ., the critical temperature being 88°C . The vapour density is 119.5, agreeing with the formula TeF_6 . The gas has an unpleasant odour, recalling ozone and tellurium hydride. Water only slowly decomposes the gas, which does not attack glass.



Tellurium Oxyfluorides.—The distant resemblance of tellurium to the metalloid antimony, its neighbour in Group VB, extends to the formation of oxyhalides or basic halides. The system $\text{TeO}_2 - \text{HF} - \text{H}_2\text{O}$ has been investigated at 10°C .⁴ and a number of crystalline hydrated oxyfluorides obtained either by slow evaporation of solutions of tellurium dioxide or tellurous acid in nearly 100 per cent. hydrofluoric acid, or by evaporation in a vacuum over concentrated sulphuric acid of solutions in 40 to 55 per cent. hydrofluoric acid. The monohydrate, $\text{TeF}_4 \cdot \text{TeO}_2 \cdot \text{H}_2\text{O}$, was generally obtained in the form of rosettes of transparent needles; the dihydrate, $\text{TeF}_4 \cdot \text{TeO}_2 \cdot 2\text{H}_2\text{O}$, sometimes separated in this form and sometimes as hard milk-white nodules of radiating crystals. An oxyfluoride of composition $2\text{TeF}_4 \cdot 3\text{TeO}_2$ was also isolated both in the anhydrous condition and as a hydrate containing $6\text{H}_2\text{O}$.

The exact nature of the oxyfluorides described has not yet been determined, but for the monohydrate there is evidence in favour of the formula $2\text{TeOF}_2 \cdot \text{H}_2\text{O}$.⁵

TELLURIUM AND CHLORINE.

Tellurium Dichloride, TeCl_2 .—This compound is the first product of the regulated action of chlorine on tellurium, but it is difficult to prevent further conversion into the tetrachloride.⁶ A more satisfactory

¹ Prideaux and Millott, *loc. cit.*

² Högbom, *Bull. Soc. chim.*, 1881, [ii.], 35, 61; Wells and Willis, *Amer. J. Sci.*, 1901, [iv.], 12, 190.

³ Prideaux, *Trans. Chem. Soc.*, 1906, 89, 316.

⁴ Prideaux and Millott, *J. Chem. Soc.*, 1926, pp. 173, 520; 1929, p. 2703.

⁵ Prideaux and Millott, *loc. cit.* See also Metzner, *loc. cit.*; Weinland and Alfa, *Zeitsch. anorg. Chem.*, 1889, 21, 43.

⁶ Berzelius, *Ann. Chim. Phys.*, 1835, 58, 113, 225; Rose, *Pogg. Annalen*, 1831, [ii.], 21, 443.

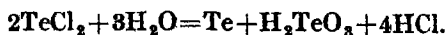
procedure is to boil tellurium tetrachloride with tellurium under reflux : ¹



When powdered tellurium is heated in a stream of carbonyl chloride, brown vapours of the dichloride are evolved, which may be condensed to a velvety-black crystalline mass.²

When in a state of fine division, tellurium dichloride has a yellowish-green colour. On account of its miscibility with tellurium the chloride is difficult to obtain pure and the recorded melting-points range from 209° to 175° C.; the boiling-point is near 324° C.³ The reddish vapour at 450° C. has a density in keeping with the unimolecular formula TeCl_2 .⁴

Bivalent tellurium is not stable and the dichloride in the solid state tends to undergo self-oxidation and reduction, forming a solid solution of the element in the tetrachloride.⁵ Under the action of water, acids or alkalis, tellurium and tellurous acid are formed :

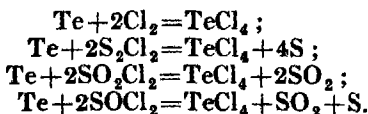


The dichloride is stable only in the gaseous condition or in solution when in equilibrium with its decomposition products.⁶ It is hygroscopic, but does not fume in air. When heated in air it burns to tellurium dioxide and tetrachloride. It is also slowly converted by chlorine into the tetrachloride.

Repeated sublimation of tellurium dichloride with a deficiency of ammonium chloride leads to the formation of a greenish-black *chlorotellurite*, $(\text{NH}_4)_2\text{TeCl}_4$, which is stable in air and not hygroscopic.⁷

The dichloride reacts with magnesium phenyl bromide, $\text{C}_6\text{H}_5\text{MgBr}$, in ether solution, with formation of diphenyl telluride, $(\text{C}_6\text{H}_5)_2\text{Te}$. Tellurium dibromide and di-iodide give a similar result.⁸ In ether solution the dichloride absorbs bromine and iodine, but the products, presumably the chlorobromide and chloro-iodide, respectively, have not been isolated.⁹

Tellurium Tetrachloride, TeCl_4 .—When chlorine is passed continually over carefully heated tellurium, the final product is a yellow liquid which solidifies to a crystalline mass on cooling. It can be purified by distillation.¹⁰ The chlorine can be replaced by sulphur monochloride,¹¹ or even by sulphuryl chloride or thionyl chloride : ¹²



¹ Michaelis, *Ber.*, 1887, 20, 2488.

² Lindner and Apolant, *Zeitsch. anorg. Chem.*, 1924, 136, 381.

³ Michaelis, *loc. cit.*

⁴ For the absorption spectrum, see Gernez, *Compt. rend.*, 1872, 74, 1190; Wöllner, *Ber.*, 1887, 20, 2490; Friederichs, *Zeitsch. wiss. Photochem.*, 1905, 3, 154.

⁵ Damiens, *Ann. Chim.*, 1923, 19, 44.

⁶ Damiens, *loc. cit.*

⁷ Lindner and Apolant, *loc. cit.*

⁸ Lederer, *Ber.*, 1915, 48, 1845.

⁹ Damiens, *loc. cit.*

¹⁰ Michaelis, *Ber.*, 1887, 20, 1780, 2488.

¹¹ Lenher, *J. Amer. Chem. Soc.*, 1902, 24, 188; MacIvor, *Chem. News*, 1902, 86, 308.

¹² von Horvath, *Zeitsch. anorg. Chem.*, 1911, 70, 408.

Tellurium dioxide is also converted into the tetrachloride by the action of sulphur monochloride or even hydrogen chloride (see p. 881).

Tellurium tetrachloride is a colourless, crystalline solid; it melts at 225°C.^1 to a yellow liquid, the colour of which deepens as the boiling-point, 390°C. , is approached. The vapour is yellow and at 440°C. has a density agreeing closely with the formula TeCl_4 , although above 500°C. appreciable dissociation occurs, probably into the dichloride and chlorine. Unlike tellurium dichloride, the vapour of which shows marked absorption bands, the vapour of the tetrachloride gives no definite absorption spectrum.²

The molten tetrachloride resembles the dichloride in readily conducting the electric current, tellurium in both cases being liberated at the cathode.

Although stable in dry air, the tetrachloride is gradually decomposed by moisture; it deliquesces, giving an oxychloride. This "oxychloride" is probably only a mixture of tetrachloride and dioxide.³ With a larger quantity of water the tetrachloride dissolves, giving rise finally to tellurium dioxide. It is soluble without decomposition in aqueous hydrochloric acid (from which an unstable compound $\text{HCl}\cdot\text{TeCl}_4\cdot 5\text{H}_2\text{O}$ crystallises at -30°C.), also in carbon disulphide and sulphur monochloride.⁴

Ammonia attacks the tetrachloride differently at various temperatures. At 200° to 250°C. reduction is effected according to the equation: ⁵



At 0°C. ammonia is absorbed, with formation of additive compounds; $\text{TeCl}_4\cdot 6\text{NH}_3$, $\text{TeCl}_4\cdot 4\text{NH}_3$ and $\text{TeCl}_4\cdot 3\text{NH}_3$ have been described.⁶ These compounds easily liberate ammonia on gently warming, and at higher temperatures form the lower chloride and ammonium chloride. Liquid ammonia (anhydrous) at still lower temperatures, *e.g.* -15°C. , converts tellurium tetrachloride into the yellow, amorphous, explosive tellurium nitride and ammonium chloride.⁷

With sulphur trioxide, tellurium tetrachloride yields a crystalline compound having the composition $\text{TeCl}_4\cdot 2\text{SO}_3$.⁸ With the chlorides of the alkali metals (including ammonium) and the organic amines, yellow tellurichlorides of the general formula X_2TeCl_6 are produced, corresponding with the unknown acid H_2TeCl_6 . These are decomposed by water with formation of tellurous acid, but can generally be recrystallised from aqueous hydrochloric acid without decomposition.⁹

When fused in a sealed tube with silver chloride the liquid separates into two layers, the lower consisting of almost pure silver chloride, whilst

¹ Simons, *J. Amer. Chem. Soc.*, 1930, 52, 3488; Biltz and Friedrich, *Zeitsch. anorg. Chem.*, 1924, 136, 416.

² Wüllner, *Ber.*, 1887, 20, 2491.

³ Lenher, *J. Amer. Chem. Soc.*, 1909, 31, 243.

⁴ Metzner, *Ann. Chim. Phys.*, 1898, [7], 15, 203.

⁵ Metzner, *loc. cit.*

⁶ Strecker and Ebert, *Ber.*, 1925, 58, [B], 2527; Wohler and Espenschied, *Annalen*, 1860, 113, 105; *J. prakt. Chem.*, 1860, 80, 430.

⁷ Metzner, *loc. cit.* See also Strecker and Ebert, *loc. cit.*

⁸ Prandtl and Borinski, *Zeitsch. anorg. Chem.*, 1909, 62, 237.

⁹ Wheeler, *Amer. J. Sci.*, 1893, [iii.], 45, 267; Lenher, *J. Amer. Chem. Soc.*, 1900, 22, 136; 1903, 25, 730; Norris and Mommers, *Amer. Chem. J.*, 1900, 23, 730; Gutbier and Flury, *J. prakt. Chem.*, 1911, [ii.], 83, 145; 1912, [ii.], 86, 150; *Zeitsch. anorg. Chem.*, 1914, 86, 180.

the upper contains $\text{AgCl}-\text{TeCl}_4$ eutectic with excess of AgCl . The eutectic melts at 210°C . and contains about 9 molecules per cent. of silver chloride.¹ Metallic silver reacts with tellurium tetrachloride to form silver telluride and chloride, excess of the tetrachloride having no further action on silver telluride; thus in its halogen compounds tellurium behaves like a "noble" metal.

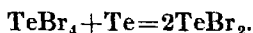
Additive compounds can be produced with aluminium chloride,² phosphorus pentachloride³ and ethyl ether,⁴ the products being $\text{TeCl}_4 \cdot 2\text{AlCl}_3$, $2\text{TeCl}_4 \cdot \text{PCl}_5$ and $\text{TeCl}_4 \cdot (\text{C}_2\text{H}_5)_2\text{O}$, respectively.⁵

Tellurium oxychloride is probably non-existent as a definite substance, the compound which has been described probably having been a mixture of chloride and oxide.⁶

Tellurium Perchlorate.—By dissolving tellurium dioxide in warm concentrated perchloric acid, a clear solution is obtained which on cooling, deposits glistening hexagonal crystals having the composition $2\text{TeO}_2 \cdot \text{HClO}_4$.⁷

TELLURIUM AND BROMINE.

Tellurium Dibromide, TeBr_2 .—Just as the tetrachloride can be reduced to the dichloride, so can tellurium tetrabromide be made to yield the dibromide by treatment in dry ether solution in the dark with finely divided tellurium. The solution so obtained is chocolate-brown in colour and is decomposed by water :⁸



The dibromide has been isolated in the solid state by rapidly cooling its vapour to -80°C . in a vacuum. It is an endothermic compound, as prepared from tellurium and its tetrabromide, and is very unstable.

As with the dichloride, the action of water even in the form of moist air, causes decomposition into the tetrahalide and free tellurium.⁹ The dibromide is completely soluble in dry ether and in such solution it will combine with iodine, forming tellurium iodobromide, which crystallises from the ether solution as red crystals.¹⁰

Tellurium Tetrabromide, TeBr_4 .—This compound can be produced by the action of excess of bromine on tellurium, the vigour of the reaction being moderated by cooling. The excess of bromine is subsequently removed by evaporation. There is a danger of the product containing a little of the dibromide or a little unaltered tellurium; it may therefore be purified by fractional sublimation under reduced

¹ Biltz and Friedrich, *loc. cit.*

² Weber, *Ann. Phys. Chem.*, 1858, [ii.], 104, 428.

³ Metzner, *loc. cit.*

⁴ Lenher, *J. Amer. Chem. Soc.*, 1900, 22, 138.

⁵ For the action of tellurium tetrachloride on diphenyl ether, see Drew, *J. Chem. Soc.*, 1926, p. 223; on aryl-alkyl ethers, see Morgan and Kellett, *ibid.*, 1926, p. 1080; Morgan and Drew, *Trans. Chem. Soc.*, 1925, 127, 2307; on monoketones, see Morgan and Elvins, *ibid.*, 1925, 127, 2625; on acetic anhydride, see Morgan and Drew, *ibid.*, p. 531; on thiocarbamide, see Falcicola, *Annali Chim. Appl.*, 1927, 17, 359.

⁶ Lenher, *J. Amer. Chem. Soc.*, 1909, 31, 243; Ditte, *Compt. rend.*, 1876, 83, 336.

⁷ Fichter and Schmid, *Zeitsch. anorg. Chem.*, 1916, 98, 141.

⁸ Damiens, *Compt. rend.*, 1921, 173, 300.

⁹ Brauner, *Monatsh.*, 1889, 10, 411.

¹⁰ Damiens, *loc. cit.*

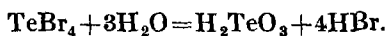
pressure, the tetrabromide being less volatile than the dibromide and more volatile than any oxybromide which may be present.¹

The same direct combination of the elements can be effected under an aqueous solution of hydrobromic acid, the resulting tetrabromide being obtained by evaporation of the solution.²

Tellurium dioxide may be converted into the tetrabromide by means of hydrobromic acid or a mixture of potassium bromide and phosphoric acid in aqueous solution.³

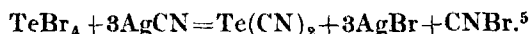
The reddish-yellow solid can be obtained in the form of prismatic needles by slow sublimation. It has a density of 4.81 and melts near 380° C. to a deep red liquid. Ebullition, which occurs near 420° C., is not effected under ordinary conditions of pressure without partial dissociation of the vapour into dibromide and bromine. The boiling-point is therefore not constant.⁴

Tellurium tetrabromide is slightly hygroscopic and can be dissolved in a little water without decomposition. The aqueous solution, on evaporation over sulphuric acid, yields a deep red hydrated product. More water causes hydrolysis to tellurous and hydrobromic acids :



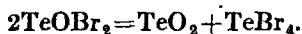
A solution of the tetrabromide in aqueous 50 per cent. tartaric acid solution becomes colourless on dilution, and the tellurium remains as tartrate.

Silver cyanide acts on a benzene solution of the tetrabromide, replacing bromine by the cyanogen radical, with simultaneous reduction, the product being a solid tellurium dicyanide :



With ammonia the tetrabromide reacts similarly to the tetrachloride,⁶ and also like the latter, it forms additive compounds with the halides of the alkali metals and ammonium and with organic bases. The *telluribromides* formed are deep red, crystalline solids, of the general formula X_2TeBr_6 ; they dissolve without decomposition in aqueous solutions of hydrobromic acid, but are decomposed more or less readily by water.⁷ The additive compound with hydrogen bromide, $\text{TeBr}_4 \cdot \text{HBr} \cdot 5\text{H}_2\text{O}$, is slightly more stable than the chlorine analogue.⁸

Tellurium Oxybromides.—Several rather indefinite oxybromide derivatives have been described. The existence of the compound TeOBr_2 , intermediate between TeBr_4 and TeO_2 , is generally recognised. On heating it first melts and then decomposes, giving a distillate of the tetrabromide :⁹



¹ Berzelius, *Ann. Chim. Phys.*, 1835, 58, 113, 225; Brauner, *loc. cit.*

² von Hauer, *J. prakt. Chem.*, 1858, 73, 98.

³ Gooch and Peirce, *Amer. J. Sci.*, 1896, [iv.], 1, 181.

⁴ Carnelley and Williams, *Trans. Chem. Soc.*, 1879, 35, 563.

⁵ Cooksedge, *ibid.*, 1908, 93, 2175.

⁶ Strecker and Ebert, *Ber.*, 1925, 58, [B], 2527.

⁷ Wheeler, *Amer. J. Sci.*, 1893, [iii.], 45, 267; Lenher, *J. Amer. Chem. Soc.*, 1900, 22, 136; 1903, 25, 730; Norris and Mommers, *Amer. Chem. J.*, 1900, 23, 486; Gutbier and Flury, *J. prakt. Chem.*, 1912, ii., 86, 150.

⁸ Metzner, *Ann. Chim. Phys.*, 1898, [vii.], 15, 203.

⁹ Ditte, *Compt. rend.*, 1876, 83, 446.

On this decomposition depends the effectiveness of the suggested method for freeing crude tellurium tetrabromide from any oxybromide present in it.

TELLURIUM AND IODINE.

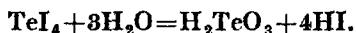
Tellurium and iodine, in the molten condition, are miscible in all proportions, and the system tellurium-iodine has been examined from the thermo-analytical standpoint, the freezing-point curve giving indications only of the formation of a tetra-iodide, TeI_4 , in the fused mixture.¹

A tellurium di-iodide has been described by Berzelius as obtained when tellurium and iodine are sublimed together, but its existence as a definite compound appears doubtful.² Damiens³ has shown that the so-called tellurium di-iodide is a mixture of the tetra-iodide and a solid solution of tellurium with the tetra-iodide.

Tellurium Tetra-iodide, TeI_4 .—This compound may be prepared in a very pure state by heating together finely divided tellurium and excess of iodine and allowing the product to cool slowly. The excess of iodine may be removed by extracting with carbon tetrachloride.⁴

The tetra-iodide may also be formed from the dioxide and concentrated hydriodic acid. Telluric acid gives a similar result. The resulting halide may separate as such or in needles of an additive compound, $\text{HI} \cdot \text{TeI}_4 \cdot 8\text{H}_2\text{O}$, which gives a residue of tetra-iodide when warmed to 50° – 60°C .⁵

The tetra-iodide forms small, brilliant, black crystals, having a density of 5.05 at 15°C . When heated above 100°C . it dissociates into tellurium and iodine. When dissolved in excess of iodine it appears probable that part of the iodide is in a bimolecular condition.⁶ It is unattacked by moist air, but is slowly decomposed by cold water, and on warming, hydrolysis occurs with the formation of an oxy-iodide of uncertain composition; on boiling with water complete hydrolysis to hydrogen iodide is effected:⁷



It is sparingly soluble in alcohol and acetone, insoluble in ether, chloroform and carbon disulphide.⁸ Alkalis and ammonia in aqueous solution readily dissolve it. It is also soluble in a solution of hydriodic acid.

Analogous with the tetrachloride and tetrabromide, additive compounds are formed by the tetra-iodide with the alkali iodides. The *telluri-iodides*,⁹ of the general formula X_2TeI_6 , are black, crystalline substances, which, like the tellurichlorides and telluribromides, generally crystallise in the regular system when anhydrous. They are decomposed

¹ Jaeger and Menke, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, 14, 724; *Zeitsch. anorg. Chem.*, 1912, 77, 320.

² Gutbier and Flury, *ibid.*, 1902, 32, 108.

³ Damiens, *Compt. rend.*, 1920, 171, 1140.

⁴ Damiens, *ibid.*, 1921, 172, 1105.

⁵ Berzelius, *Ann. Chim. Phys.*, 1835, 58, 113, 225.

⁶ Beckmann, *Sitzungsber. K. Akad. Wiss. Berlin*, 1913, p. 886; Beckmann and Hanslian, *Zeitsch. anorg. Chem.*, 1913, 80, 221.

⁷ Gutbier and Flury, *loc. cit.*

⁸ Damiens, *loc. cit.*

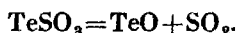
⁹ Wheeler, *Amer. J. Sci.*, 1893, [iii.], 45, 267; *Zeitsch. anorg. Chem.*, 1893, 3, 428.

by water in the same way as the tetra-iodide, although they are soluble without decomposition in concentrated hydriodic acid. It has not been found possible to obtain the corresponding di-hydrogen tellurium hexa-iodide. By the interaction of tellurium tetra-iodide, iodine and hydriodic acid in a sealed tube, the only product is a substance having the composition $\text{TeI}_4 \cdot \text{HI} \cdot 8\text{H}_2\text{O}$.¹

TELLURIUM AND OXYGEN.

Three oxides are known, the lowest being relatively unimportant.

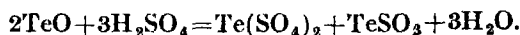
Tellurium Monoxide or Tellurium Suboxide, TeO , is produced when tellurium-sulphur sesquioxide (see p. 389) is heated in a vacuum at 180° to 225°C ., the residue being washed with sodium carbonate solution, hot water and finally alcohol :²



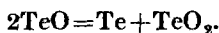
According to Damiens,³ however, the substance obtained is a mixture of tellurium and tellurium dioxide.

In dry air tellurium monoxide is a stable, amorphous, grey powder, or a porous solid, to which a graphitic lustre can be imparted by pressure. It is slowly oxidised in moist air and also when heated in dry air, being converted into the dioxide.

Oxidising agents such as nitric acid and potassium permanganate convert the monoxide into the dioxide. Concentrated sulphuric acid has a somewhat similar effect, the red solution primarily produced slowly depositing tellurium sulphate :



Compared with tellurium and tellurium dioxide, tellurium monoxide is relatively unstable, as can be shown by the ease with which it passes into these two substances, for example when heated strongly in a vacuum or when treated with dilute acids or alkalis :



The monoxide absorbs gaseous hydrogen chloride without any marked change in appearance, but on heating some tellurium dichloride sublimes ; the direct relationship between these two compounds is thus demonstrated.

Tellurium Dioxide, TeO_2 .—As has already been mentioned, tellurium burns in air with the formation of the dioxide.

The oxidation can also be effected in the wet way, for example by the gradual addition of finely divided tellurium (preferably precipitated) to excess of nitric acid. A basic tellurium nitrate is the primary product (see later, p. 390), but on suitably diluting with water, tellurium dioxide is obtained as a colourless, crystalline precipitate.⁴ An

¹ Menke, *Zeitsch. anorg. Chem.*, 1912, 77, 282 ; Metzner, *Ann. Chim. Phys.*, 1898, [vii.], 15, 203.

² Weber, *J. prakt. Chem.*, 1882, [ii.], 25, 218 ; Divers and Shimosé, *Trans. Chem. Soc.*, 1883, 43, 319 ; Ber., 1883, 16, 1004 ; Doolan and Partington, *Trans. Chem. Soc.*, 1924, 125, 1402.

³ Damiens, *Compt. rend.*, 1924, 179, 829.

⁴ Berzelius, *Ann. Chim. Phys.*, 1835, [ii.], 58, 43, 225 ; Klein and Morel, *ibid.*, 1885, [vi.], 5, 59 ; Browning and Flint, *Amer. J. Sci.*, 1909, [iv.], 28, 112.

alternative procedure is to evaporate the nitric acid solution and ignite the residue.¹

Tellurium dioxide is known in two different crystalline forms. Crystals of the tetragonal system,² but almost regular ($a:c=1:1.1076$), of density 5.66, are obtainable from the solution in nitric acid, while the molten dioxide when slowly cooled deposits rhombic needles³ ($a:b:c=0.4566:1:0.4693$) of density 5.93 and identical with the rarely occurring mineral *tellurite*.

The formation of tellurium dioxide from tellurium and oxygen is attended, according to Mixer, by the evolution of 87,100 calories per gram-molecular weight.⁴ Schuhmann⁵ gives the heat of formation at 25° C. as 77,700 calories and the free energy of formation as -64,820 calories.

When heated, the dioxide fuses at an incipient red heat, giving a clear, deep yellow liquid, the colour being lost on cooling. On account of its considerable latent heat of fusion, the mass becomes feebly incandescent during solidification. Appreciable volatilisation occurs at 400° to 500° C., the oxide, however, being much less volatile than tellurium itself.

Tellurium dioxide is very sparingly soluble in water (1 part in 150,000 at the ordinary temperature). The solution has no acidic properties. The presence of even small quantities of nitric acid raises the solubility, on account of the formation of a basic nitrate, hot dilute solutions of which, however, frequently deposit the dioxide in a crystalline form on cooling.⁶ It is also soluble in diluted sulphuric acid, owing to the formation of basic telluric sulphate.⁷

The dioxide can be reduced to tellurium by heating with carbon or with potassium cyanide.⁸ A similar result can be produced by heating in a current of hydrogen, but the temperature required is high.⁹

For the reduction of tellurium dioxide in alkaline or acid solution, see later.

When heated in sulphur monochloride vapour, tellurium dioxide is readily attacked with formation of tellurium tetrachloride or dichloride, according as to whether the sulphur monochloride or the tellurium dioxide is present in excess.¹⁰

Aqueous solutions of the alkali hydroxides readily dissolve tellurium dioxide with formation of the corresponding tellurite. In the presence of hydrogen peroxide the corresponding tellurate is formed.¹¹ Ammonia and the alkali carbonates in cold aqueous solution have little effect, but the latter in hot solution or in the fused condition give rise to tellurites. Nitrates of the alkali metals on fusion with tellurium dioxide produce tellurates.¹²

¹ Wills, *Annalen*, 1880, 202, 246.

² Klein and Morel, *Ann. Chim. Phys.*, 1885, [vi.], 5, 69; 1887, 10, 108; Urba, *Zeitsch. Kryst. Min.*, 1891, 19, 1.

³ Schafarik, *J. prakt. Chem.*, 1863, 90, 13; Brezina, *Zeitsch. Kryst. Min.*, 1888, 13, 610; Clarke, *Amer. J. Sci.*, 1877, [iii.], 14, 286.

⁴ Schuhmann, *J. Amer. Chem. Soc.*, 1925, 47, 356.

⁵ Dudley and Bowers, *ibid.*, 1913, 35, 875; Klein and Morel, *loc. cit.*

⁶ Brauner, *Monatsh.*, 1891, 12, 34. ⁷ Rose, *Ann. Phys. Chem.*, 1861, [ii.], 112, 308.

⁸ Staudenmaier, *Zeitsch. anorg. Chem.*, 1895, 10, 197.

⁹ Lenher, *J. Amer. Chem. Soc.*, 1908, 30, 737.

¹⁰ Guttier and Wagenknecht, *Zeitsch. anorg. Chem.*, 1904, 40, 263.

¹² Berzelius, *Ann. Chim. Phys.*, 1835, [ii.], 58, 43, 225.

Tellurium Dioxide as a Base.—Tellurium dioxide possesses definite basic tendencies, the tellurium being capable of acting as a quadrivalent atom and the group TeO , telluryl, as a bivalent basic radical.

When heated in a current of dry hydrogen chloride¹ or with solid ammonium chloride,² tellurium dioxide forms the tetrachloride. With hydrogen chloride at low temperatures several workers³ have reported the formation of additive compounds similar to those obtained with selenium dioxide (see p. 325); these at higher temperatures yield water and the tetrachloride. Parker and Robinson,⁴ however, in a recent investigation find no evidence that tellurium dioxide forms any definite addition compound up to 150°C .; at 0°C . hydrogen chloride is absorbed to give a product obviously not homogeneous, which loses water continuously with rise in temperature, and probably consists of basic chlorides. The formation of the tetrabromide by the interaction of tellurium dioxide and hydrogen bromide has already been described (p. 377). Reference has also just been made to the solubility of the dioxide in sulphuric acid and in nitric acid, the description of the resulting basic sulphate and nitrate being given later (pp. 389, 390).

The salts of basic tellurium are colourless and are easily hydrolysed in dilute aqueous solution with formation of the dioxide. The addition of tartaric acid checks the separation of the dioxide on account of the formation of the stable acid tellurium tartrate $\text{Te}(\text{HC}_4\text{H}_4\text{O}_6)_4$,⁵ which can be obtained in the crystalline condition, as also can the silver telluryl tartrate $\text{Ag}_2(\text{TeO})(\text{C}_4\text{H}_4\text{O}_6)_2$, analogous to potassium antimonyl tartrate.⁶

Aqueous solutions of the salts, or of tellurium dioxide in acids, easily undergo reduction to elementary tellurium. Phosphorus, phosphorous acid,⁷ hypophosphorous acid,⁸ sulphurous acid,⁹ thiosulphuric acid,¹⁰ hyposulphurous acid,¹¹ hydriodic acid,¹² hydrogen sulphide,¹³ ferrous salts, stannous salts,¹⁴ hydrazine¹⁵ and phenylhydrazine, as well as various metals,¹⁶ e.g. zinc, iron, tin, cadmium, antimony and copper, are able to effect this reduction.

By treatment with sufficiently strong oxidising agents, such as chromic acid or potassium permanganate with hydrochloric or sulphuric acid, aqueous solutions of salts of basic tellurium are converted into solutions of telluric acid.¹⁷

¹ Berg, *Bull. Soc. chim.*, 1905, [iii.], 33, 1310.

² Gutbier and Flury, *Zeitsch. anorg. Chem.*, 1903, 37, 152.

³ Ditte, *Compt. rend.*, 1876, 83, 336; Lenher, *J. Amer. Chem. Soc.*, 1909, 31, 243.

⁴ Parker and Robinson, *J. Chem. Soc.*, 1928, p. 2853.

⁵ Becker, *Annalen*, 1876, 180, 262.

⁶ Klein, *Ann. Chim. Phys.*, 1887, [vi.], 10, 14; Brauner, *Monatsh.*, 1889, 10, 434; Becker, *loc. cit.*

⁷ Rose, *Ann. Phys. Chem.*, 1861, [ii.], 112, 307.

⁸ Gutbier, *Zeitsch. anorg. Chem.*, 1902, 32, 295.

⁹ Donath, *Zeitsch. angew. Chem.*, 1890, 4, 215.

¹⁰ Gooch and Howland, *Zeitsch. anorg. Chem.*, 1894, 7, 132.

¹¹ Donath, *loc. cit.*

¹² Gooch and Howland, *loc. cit.*

¹³ Gutbier and Flury, *Zeitsch. anorg. Chem.*, 1902, 32, 272.

¹⁴ Fischer, *Ann. Phys. Chem.*, 1828, [ii.], 13, 257; Brauner, *Monatsh.*, 1890, 11, 527.

¹⁵ Gutbier and Flury, *loc. cit.*

¹⁶ Fischer, *Ann. Phys. Chem.*, 1828, [ii.], 12, 502. For the suggested use of tellurium dioxide as an oxidising agent for such materials as hard steels and ferro-chrome alloys, see Glauser, *Chem. Zeit.*, 1914, 38, 187.

¹⁷ Brauner, *Monatsh.*, 1890, 11, 532; 1891, 12, 31.

Tellurium Dioxide as an Acid Anhydride.—When tellurium tetrachloride is treated with water, or when an aqueous solution of a tellurium salt is decomposed by an aqueous alkaline solution, a bulky, colourless precipitate is obtained which is sufficiently soluble in water to impart an acid reaction to the solution and which is more readily soluble than tellurium dioxide in acids or alkalis. A similar precipitate is obtained on acidifying a cold aqueous solution of potassium tellurite with a slight excess of nitric acid. This product is a *tellurous acid*, possibly H_2TeO_3 , but it is very unstable and spontaneously dehydrates, slowly at the ordinary temperature and rapidly at 40°C . with formation of dioxide.¹

Tellurous acid can be prepared from the residues from the electrolytic refining of copper by treating them with a solution of ammonia. On the addition of acetic acid to the resulting solution tellurous acid is obtained as a precipitate. When this precipitation is carried out in the cold the product obtained is readily soluble in alkali hydroxide, but if the precipitation takes place in a hot solution the product tends to be insoluble in the alkali hydroxides.²

The concentration of tellurous cation in solutions containing increasing amounts of hydrochloric acid has been determined by potential measurements, using a tellurium electrode, the total tellurium content of the solutions being determined chemically.³ The concentration of the tellurium ion was found to increase as the fourth power of the concentration of the hydrogen ions, the relation being in accordance with the expression

$$[\text{Te} \cdot][\text{OH}']^4/[\text{H}_2\text{TeO}_3] = 1.5 \times 10^{-46}.$$

This is in agreement with the behaviour of tellurous acid as a weak base.

Tellurites.—The alkali tellurites are obtainable from the dioxide by treatment with an aqueous solution of an alkali hydroxide or carbonate or by fusion with an alkali carbonate. They are soluble in water and the other tellurites can be prepared from them by precipitation, those of the alkaline earths being sparingly soluble, the remainder even more sparingly soluble.

In composition, the salts are not all closely related to the monohydrated acid, H_2TeO_3 , although many are derived from this acid. Other salts are known⁴ which appear to be derived from hypothetical condensed acids of composition $\text{H}_2\text{Te}_2\text{O}_6$, *ditellurous acid*, and $\text{H}_2\text{Te}_4\text{O}_9$, *tetratellurous acid*, which may be regarded as products of the partial dehydration of the normal acid, H_2TeO_3 , or as intermediate products in the hydration of tellurium dioxide.

The tellurites in aqueous solution are not very stable, being decomposed by hydrogen sulphide⁵ or atmospheric carbon dioxide and undergoing oxidation when treated with oxidising agents such as the permanganates, the halogens or hydrogen peroxide, with formation of tellurates.⁶

¹ Berzelius, *loc. cit.*

² Oberhelman and Browning, *Amer. J. Sci.*, 1913, [iv.], 36, 399.

³ Kasarnowsky, *Zeitsch. physikal. Chem.*, 1924, 109, 287.

⁴ See, for example, Lenher and Wolesensky, *J. Amer. Chem. Soc.*, 1913, 35, 718.

⁵ MacIvor, *Chem. News*, 1903, 87, 209.

⁶ Brauner, *Monatsh.*, 1891, 12, 44; Gooch and Howland, *Zeitsch. anorg. Chem.*, 1894, 7, 134.

They are also reducible to tellurium by dextrose,¹ by sodium hydro-sulphite² and by electrolysis.³

On heating to a temperature of 440° to 470° C. in air, tellurites undergo oxidation, although under these conditions tellurium dioxide is not oxidised nor do the tetratellurites undergo oxidation. In the case of potassium ditellurite the oxidation results in the formation of a compound having the composition $K_2O \cdot TeO_3 \cdot TeO_2$.

With the exception of magnesium tellurite the precipitated tellurites are flocculent and show no tendency to crystallise. The following tellurites have been prepared :⁴

Barium Tellurite, obtained by precipitation from barium chloride solution ; the precipitate appears to occlude large quantities of the chloride.

Cadmium Tellurite, $3CdTeO_3 \cdot 2H_2O$.

Cobalt Tellurite, $CoTeO_3 \cdot H_2O$.

Lead Tellurite, $3PbTeO_3 \cdot 2H_2O$.

Magnesium Tellurite, $5MgTeO_3 \cdot 9H_2O$ and $10MgTeO_3 \cdot 9H_2O$.

Manganous Tellurite.—This salt is readily oxidised by the air at ordinary temperatures to the manganic state.

Nickel Tellurite, $NiTeO_3 \cdot 2H_2O$.

Potassium Tellurite, $K_2TeO_3 \cdot 3H_2O$; *Potassium Ditellurite* ; *Potassium Tetratellurite*, $K_2Te_4O_9 \cdot 4H_2O$.

Silver Tellurite, obtainable in several varieties, differing in colour.

Sodium Tellurite, $Na_2TeO_3 \cdot 5H_2O$; *Sodium Ditellurite* ; *Sodium Tetratellurite*, $Na_2Te_4O_9 \cdot 4H_2O$.

The ammonium salt could not be isolated. A *copper ammonium tellurite* of composition $TeO_2 = 88.84$, $CuO = 4.68$, $NH_3 = 5.22$, $H_2O = 6.10$ per cent. has been obtained.⁵

Tellurium Trioxide, TeO_3 .—This, like so many of the tellurium compounds, was discovered by Berzelius. It is formed when telluric acid is heated a little above 360° C. Care is necessary, since overheating induces decomposition of the yellow trioxide into the colourless dioxide. Any dioxide that forms can be removed by treating with concentrated hydrochloric acid, in which the trioxide is only sparingly soluble.⁶

Tellurium trioxide is an orange-yellow solid, of density 5.10 at the ordinary temperature.⁷ Its heat of formation per gram-molecular weight is 83.6 Calories,⁸ and according to Mixter the decomposition of the trioxide into the dioxide is an exothermic reaction (*cf.* p. 380). As might therefore be expected, this decomposition occurs readily and at such a temperature that the resulting dioxide is unfused.

The trioxide is insoluble in water, hot or cold, in nitric acid and in cold hydrochloric acid. Concentrated hydrochloric acid when heated attacks it with liberation of chlorine and formation of tellurium tetrachloride in the solution. The caustic alkalis only dissolve tellurium trioxide in hot concentrated solution, with formation of tellurates.

¹ Stolba, *Zeitsch. anal. Chem.*, 1872, 11, 437.

² Brunck, *Annalen*, 1904, 336, 281.

³ Müller, *Ber.*, 1903, 36, 4262.

⁴ Lenher and Wolesensky, *loc. cit.*

⁵ Oberhelman and Browning, *loc. cit.*

⁶ Berzelius, *Ann. Chim. Phys.*, 1835, 58, 113, 225 ; Staudenmaier, *Zeitsch. anorg. Chem.*, 1895, 10, 189.

⁷ Clarke, *Amer. J. Sci.*, 1877, [iii.], 14, 286.

⁸ Mixter, *ibid.*, 1910, [iv.], 29, 488.

Telluric Acids and the Tellurates.

Tellurium trioxide gives rise to several hydration products which can all be regarded as telluric acids, but which are more conveniently considered as products of the further hydration of telluric acid, H_4TeO_4 , the compound $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ (possibly an "ortho-" telluric acid, H_6TeO_6 , see p. 387) being the most stable.

Formation and Preparation.—(1) Powerful oxidising agents are able to convert tellurium into the sexavalent condition, the product obtained in the presence of water being telluric acid, whereas in the presence of an alkali a tellurate is obtained.

(a) Aqua regia oxidises tellurium, incompletely, as far as telluric acid. Nitric acid gives a solution of tellurous acid, which by the action of lead dioxide¹ or chromium trioxide² produces telluric acid.

(b) A still better process is the passage of chlorine into an aqueous suspension of tellurium until the clear solution no longer gives a precipitate of tellurous acid when made alkaline and subsequently acidified with acetic acid.³ The solution obtained, when evaporated to small bulk and treated with alcohol, gives a crystalline precipitate of the compound $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$.

(c) Sodium peroxide oxidises an aqueous suspension of tellurium to sodium tellurate.⁴

(2) Instead of using tellurium as the starting-point, the dioxide can be employed, either as such or in the form of tellurite. Method (1) (a) involves such oxidation of the dioxide, which is formed as an intermediate product. The dioxide can also be oxidised by fusing with potassium nitrate⁵ or potassium chlorate;⁶ it can also be replaced for this purpose by a tellurite; the product in each case is a tellurate, from which the free acid is obtainable by precipitation as barium tellurate and treatment of this with the calculated quantity of sulphuric acid. The oxidation of the alkali tellurite can be effected still more satisfactorily in solution by hydrogen peroxide; in this case the relative amount of alkali metal present is so small that the concentrated solution on acidification with nitric acid deposits crystals of the acid, $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$, which can be recrystallised from a little water, separation being aided by the addition of nitric acid.⁷

(3) A very pure product and almost theoretical yield may be obtained by the oxidation of tellurium tetrachloride with chloric acid. A slight excess of chloric acid is used to avoid the formation of any explosive oxides of chlorine. The addition of concentrated nitric acid causes precipitation of the telluric acid, which may be freed from chlorine and nitrogen oxides by drying in a vacuum. Prepared by this method the acid has the composition $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$.⁸

Properties.—Two different crystalline forms of the dihydrate,

¹ Becker, *Annalen*, 1876, 180, 257.

² Staudenmaier, *Zeitsch. anorg. Chem.*, 1895, 10, 189; Gutbier, *ibid.*, 1902, 32, 96.

³ Browning and Minnig, *Amer. J. Sci.*, 1913, [iv.], 36, 72.

⁴ Köthner, *Annalen*, 1901, 319, 1.

⁵ Berzelius, *Ann. Chim. Phys.*, 1835, 58, 113, 225; Lenher and Potter, *J. Amer. Chem. Soc.*, 1909, 31, 24.

⁶ Oppenheim, *J. prakt. Chem.*, 1857, 71, 266.

⁷ Gutbier and Wagenknecht, *Zeitsch. anorg. Chem.*, 1904, 40, 260; Gutbier and Resensoeck, *ibid.*, 1904, 42, 174. See also Mathers and Bradbury, *J. Amer. Chem. Soc.*, 1929, 51, 3229.

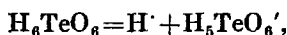
⁸ Meyer and Moldenhauer, *Zeitsch. anorg. Chem.*, 1921, 119, 132.

$\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$, are known. The acid separating from hot concentrated solution in nitric acid crystallises in octahedra¹ of the regular system, having a density of 3.085. The more usual and more stable form consists of prismatic crystals of the monoclinic system, having a density of 3.071, and obtained on gradual evaporation of an aqueous solution or on cooling a dilute solution in warm dilute nitric acid.²

By very cautious heating at 140° C. the dihydrate very gradually loses a bimolecular proportion of water, forming *allotelluric acid*, H_2TeO_4 , which is a loose powder of density 3.48 at 19° C.;³ on further heating it passes successively into tellurium trioxide and tellurium dioxide.

The dihydrated acid is a snow-white crystalline powder, easily soluble in water⁴ but not deliquescent. The addition of nitric acid or of alcohol diminishes its solubility in water. When its aqueous solution is evaporated at 0° C., tetragonal crystals of a *hexahydrate*, $\text{H}_2\text{TeO}_4 \cdot 6\text{H}_2\text{O}$, are obtained.⁵

In aqueous solution the acid has a metallic taste and only feebly affects litmus; the latter characteristic is in accord with the evidence of its electrical conductivity, which is small and indicates relatively slight dissociation, comparable with that of hydrogen sulphide rather than with that of sulphuric acid. Measurements of the hydrogen-ion concentration of normal telluric acid solution gave $[\text{H}^+] = 4 \times 10^{-5}$ gram-ion per litre. On the assumption that the acid is ionised in accordance with the equation (see p. 387)



this gives the ionisation constant $K = 1.6 \times 10^{-4}$. According to this result telluric acid is a very weak acid.⁶

Examination of the solubility curves of the dihydrate and the hexahydrate shows that these intersect at 10° C.; this temperature therefore is the highest at which the hexahydrate is stable with reference to the dihydrate.⁷ The heat of solution of the dihydrate is negative,⁸ the value per gram-molecule being -3.35 Calories.

Allotelluric acid, H_2TeO_4 , judged by its electrical conductivity in aqueous solution, is a decidedly stronger acid than the dihydrate, $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$, but in the course of three days conversion into the latter acid is complete. Cryoscopic examination of the aqueous solution shows that the molecule of allotelluric acid is more complex than that of the dihydrate, the change $(\text{H}_2\text{TeO}_4)_x \longrightarrow \text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ being one of concurrent depolymerisation and hydration.⁹ It has been suggested¹⁰ that allotelluric acid is not a homogeneous substance, but a mixture of polymerised forms of the crystalline acid.

¹ On the crystal structure of telluric acid, see Kirkpatrick and Pauling, *Zeitsch. Krist.*, 1926, 63, 502.

² Gosaner, *Zeitsch. Krist. Min.*, 1903, 38, 498; Gutbier and Gossner, *Chem. Zentr.*, 1906, i., 635.

³ Clarke, *Amer. J. Sci.*, 1878, [iii.], 16, 401.

⁴ For a method of determining the concentration of aqueous solutions of telluric acid by means of an immersion refractometer, see Urban and Meloche, *J. Amer. Chem. Soc.*, 1928, 50, 3003.

⁵ Staudenmaier, *Zeitsch. anorg. Chem.*, 1895, 10, 189.

⁶ Rosenheim and Jander, *Kolloid-Zeitsch.*, 1918, 22, 23.

⁷ Mylius, *Ber.*, 1901, 34, 2214.

⁸ Metzner, *Ann. Chim. Phys.*, 1898, [vii.], 15, 203.

⁹ Mylius, *loc. cit.*

¹⁰ Rosenheim and Jander, *loc. cit.*

Telluric acid (dihydrate), when heated, loses water and becomes orange in colour, then gradually changing to white, owing to the successive formation of trioxide and dioxide. The residue is soluble in hydrochloric acid, forming an amber-coloured solution.

Telluric acid may readily be reduced, although not so easily as selenic acid. Hydrochloric acid on warming effects a partial reduction to the dioxide, and on boiling, chlorine is evolved; the latter reaction is characteristic of tellurium in the sexavalent form.¹ Hydrobromic and hydriodic acids can carry the reduction to tellurium.² Anhydrous hydrogen chloride converts heated telluric acid into tellurium tetrachloride, which sublimes away from the heated mass.³ Sulphurous acid causes a partial reduction to tellurium.⁴ Hypophosphorous acid and hydrazine can effect quantitative reduction to tellurium.⁵ The reducing action of hydrogen sulphide on telluric acid may be due to the formation of unstable sulphonyltelluric acid, which breaks down with the liberation of tellurium and sulphur.⁶ Telluric acid in 80 per cent. solution is reduced to tellurous acid by sulphur, selenium or tellurium.⁷

A concentrated solution of telluric acid boiled with a solution of potassium thiocyanate yields a yellow, heterogeneous, amorphous precipitate, containing tellurium, carbon and nitrogen.⁸

Possibly owing to its oxidising power, telluric acid in warm aqueous solution is more active towards metals than might be expected from its feeble acidity, even lead, tin, silver and mercury being attacked.⁹

Telluric acid is able to form well-defined crystalline additive compounds with the salts of such acids as iodic, arsenic, phosphoric, molybdic and tungstic acids. It also forms large, well-defined crystals with potassium nitrate of the composition $2\text{KNO}_3 \cdot \text{H}_2\text{TeO}_4 \cdot 4\text{H}_2\text{O}$. With silver nitrate telluric acid forms the compound $\text{AgNO}_3 \cdot \text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$.

When telluric acid or an alkali tellurate, or even tellurium dioxide, is heated with ammonium chloride, the mixture changes in colour from yellow to orange with the formation of a white sublimate. On further heating the mixture darkens in colour, while a yellow sublimate is formed which in turn blackens on careful heating. If the chloride is replaced by other common salts of ammonium, such as the nitrate, carbonate, sulphate, phosphate, acetate or molybdate, these changes do not occur. It has been suggested¹⁰ that the white sublimate consists partly of ammonium chloride and partly of the additive product $\text{TeO}_2 \cdot 2\text{HCl}$, and that the black sublimate is probably an ammoniated tellurous chloride, possibly $\text{TeCl}_2 \cdot 2\text{NH}_3$.

Solutions of telluric acid give a quantitative precipitation of barium tellurate, $\text{BaTeO}_4 \cdot 3\text{H}_2\text{O}$, on the addition of barium hydroxide solution, and the use of a standard barium hydroxide solution, followed by titration of the excess of alkali with a standard solution of oxalic acid, using phenolphthalein as indicator, forms a convenient process for

¹ Gutbier and Wagenknecht, *Zeitsch. anorg. Chem.*, 1904, 40, 260.

² Gooch and Howland, *Amer. J. Sci.*, 1894, [iii.], 48, 375.

³ Berg, *Bull. Soc. chim.*, 1905, [iii.], 33, 1310.

⁴ Brauner, *Trans. Chem. Soc.*, 1895, 67, 547.

⁵ Gutbier, *Ber.*, 1901, 34, 2724; *Zeitsch. anorg. Chem.*, 1902, 32, 295.

⁶ Brauner, *loc. cit.*

⁷ Benger, *J. Amer. Chem. Soc.*, 1917, 39, 2179.

⁸ Gutbier, *Zeitsch. anorg. Chem.*, 1902, 32, 31.

⁹ Hutchins, *J. Amer. Chem. Soc.*, 1905, 27, 1157.

¹⁰ Gutbier and Flurv. *Zeitsch. anorg. Chem.*, 1903, 37, 152.

the determination of the acid.¹ With a solution of mercurous nitrate telluric acid and the tellurates yield a yellow crystalline precipitate of mercurous tellurate; the crystals may either take the form of triclinic plates or spheroidal masses.²

The oxyacids of tellurium, like those of selenium, have an inhibitory action on the growth of many bacilli in cultures. The ions of selenious and tellurous acids seem to be much more inhibitory than those of selenic and telluric acids. In the case of the growth of diphtheria bacilli³ it has been shown that the active concentrations of selenium and tellurium are, for selenites, 1 : 1160, for selenates, 1 : 666, for tellurites, 1 : 420, and for tellurates, 1 : 125.⁴

The Tellurates.—It is an interesting fact that tellurium dioxide dissolves in a solution of telluric acid; the solution on slow evaporation gives crystals of telluric acid together with granules of a tellurium tellurate, $2\text{TeO}_2 \cdot \text{TeO}_3$ or Te_3O_7 .⁵

Although it can be completely neutralised by alkali hydroxides, telluric acid is so weak that with cold solutions of the alkali carbonates only acid salts of the type KHTeO_4 are produced, the solutions of which are alkaline in reaction.

The frequent presence of two molecules of water of crystallisation in the normal salts of the "normal" acid, for example $\text{Ag}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$, $\text{HgTeO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{K}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$,⁶ serves as a confirmation of the suggested existence of an *orthotelluric acid*, H_6TeO_6 , of which such compounds can be regarded as acid salts; indeed such salts as Hg_6TeO_6 and Cu_3TeO_6 may be considered to be normal salts of this acid, although on the other hand they may be classed as basic salts of the acid H_2TeO_4 .

The fact that the dihydrate in aqueous solution is a much weaker acid than sulphuric acid (see p. 385) may be cited as evidence that the two acids are materially different in nature, and this supports the view that the dihydrate in solution is actually orthotelluric acid.

The ordinary tellurates of colourless metallic radicals are colourless substances. The salts of the alkali metals are soluble in water but have no definite solubility. In many respects these salts resemble colloids, many of the basic and so-called acid salts which have been described having been shown to be adsorption compounds.⁷ When the alkali tellurates are heated, they decompose with the formation of tellurites, and they are generally more easily reducible than the latter salts.

In addition to the afore-named classes of salts, *pyrotellurates*, such as NaHTe_2O_7 , can be obtained by the action of the calculated quantities of alkali carbonate or hydroxide on ordinary telluric acid. When heated, these pyrotellurates, which are colourless, soluble salts, eliminate the elements of water :



The resulting *tetratellurates* or *anhydrotellurates* are very sparingly soluble yellow solids, and it has been suggested (by Berzelius) that the

¹ Rosenheim and Weinheber, *Zeitsch. anorg. Chem.*, 1911, 69, 286.

² Denigès, *Ann. Chim. anal.*, 1915, 20, 57.

³ Joachimoglu and Hirose, *Biochem. Zeitsch.*, 1921, 125, 1.

⁴ See also Joachimoglu, *ibid.*, 1920, 107, 300.

⁵ Metzner, *Ann. Chim. Phys.*, 1898, [vii.], 15, 203.

⁶ Hutchins, *J. Amer. Chem. Soc.*, 1906, 27, 1157.

⁷ Rosenheim and Jander, *Kolloid-Zeitsch.*, 1918, 22, 23.

yellow insoluble tetratellurates are closely related to the yellow insoluble tellurium trioxide, whilst the colourless ordinary tellurates are to be referred to the colourless soluble telluric acid. On boiling with nitric acid, the tetratellurates are converted into the soluble colourless tellurates. Potassium tetratellurate may also be obtained by fusion of tellurous acid or an alkali tellurite with potassium nitrate. On cooling, the mass is extracted with water, and the tetratellurate, $K_2Te_4O_{18}$, remains behind as an insoluble powder. On reduction of this salt with nascent hydrogen, for example by suspending the powder in dilute hydrochloric acid and adding zinc, elementary tellurium is obtained as a black powder.¹

That the foregoing classes of salts may be derived from different acids is quite feasible, for the second form of telluric acid described, *allotelluric acid*, obtained by heating the crystalline acid H_6TeO_6 (p. 385), differs from the ortho-acid not only in its greater acidity but in its precipitation reactions.²

It is evident that telluric acid is notably different from what might be expected by analogy with sulphuric and selenic acids. One is hardly surprised, therefore, that isomorphism is exceedingly rare between the tellurates and the sulphates or selenates.³ The tellurates do not form alums, they do not as a rule form mixed crystals with the sulphates or selenates, the only fairly satisfactory case of mixed-crystal formation being with rubidium hydrogen sulphate and rubidium hydrogen tellurate.

This exceptional behaviour of the tellurates is one of the arguments used by those chemists who wish to place tellurium elsewhere than in the sulphur group of elements.

Tellurates of organic bases have been described,⁴ for example carbamide tellurate, $CO(NH_2)_2 \cdot H_2TeO_4 \cdot 0.5H_2O$; thiocarbamide tellurate, $CS(NH_2)_2 \cdot 4H_2TeO_4$; hexamethylenetetramine tellurate, $(CH_2)_6N_4 \cdot H_2TeO_4 \cdot 4H_2O$; and piperazine tellurate, $C_4H_{10}N_2 \cdot 2H_2TeO_4 \cdot 4H_2O$.

Chromotellurates, $2R_2O \cdot 4CrO_3 \cdot TeO_3$, of sodium, potassium and ammonium have been prepared⁵ by spontaneous evaporation of an aqueous solution containing the corresponding dichromate (1 mol.), chromium trioxide (2 mols.) and telluric acid (1 mol.). Two ammonium molybdotellurates, $3(NH_4)_2O \cdot 6MoO_3 \cdot TeO_3 \cdot 7H_2O$ and $3(NH_4)_2O \cdot 6MoO_3 \cdot 2TeO_3 \cdot 10H_2O$, have also been obtained.⁶ Guanidinium salts of the molybdotelluric acid and of the corresponding tungstotelluric acid have been prepared,⁷ and have been formulated in accordance with Rosenheim's views on the constitution of such heteropoly-acids (see this series, Vol. VII., Part III., p. 164): $(CN_3H_6)_6[Te(MoO_4)_6] \cdot 6H_2O$ and $(CN_3H_6)_6[Te(WO_4)_6] \cdot 3H_2O$.

TELLURIUM AND SULPHUR.

Tellurium Disulphide, TeS_2 .—When hydrogen sulphide is passed into a solution of tellurium dioxide or into an acidified solution of a

¹ Hulot, *Bull. Soc. chim.*, 1920, [iv.], 27, 33.

² Mylius, *Ber.*, 1901, 34, 2214.

³ Pellini, *Atti R. Accad. Lincei*, 1906, [v.], 15, i., 629, 711; 1909, [v.], 18, ii., 279.

⁴ Greenbaum, *Amer. J. Pharm.*, 1928, 100, 630.

⁵ Berg, *Compt. rend.*, 1911, 152, 1587; *Bull. Soc. chim.*, 1911, [iv.], 9, 583.

⁶ Meloche and Woodstock, *J. Amer. Chem. Soc.*, 1929, 51, 171.

⁷ Rosenheim and Weinheber, *Zeitsch. anorg. Chem.*, 1910, 69, 261, 266; Haeblerle, *Dissertation* (Berlin, 1911), p. 14.

tellurite at room temperature, a reddish-brown precipitate is obtained having the composition TeS_2 . There has been much doubt expressed, however, as to whether tellurium sulphide is a true compound or merely a mixture of the elements, since the sulphur is extractable by carbon disulphide.

Hageman¹ has shown that below -20°C . the disulphide is stable, but that dissociation takes place at about that temperature, the degree increasing with rise in temperature; the degree of dissociation at any temperature may, of course, be determined by the amount of extractable sulphur present. The stability of the compound is then solely a matter of temperature.²

Hageman³ has also shown that the compound TeS suggested by Snelling⁴ does not exist.

The existence of a trisulphide, TeS_3 , produced by the action of hydrogen sulphide on a solution of telluric acid, is improbable, the product behaving like a mixture containing free sulphur and tellurium.

Tellurium and sulphur do not combine when fused together, but are miscible in all proportions in the molten condition (see p. 358).

Certain unstable *thiotellurites* have been prepared by the action of hydrogen sulphide on solutions of alkali tellurites, the most definite being the *potassium salt*, K_2TeS_3 .⁵

Tellurium-Sulphur Sesquioxide or Tellurium Sulphoxide, TeSO_3 .—As mentioned already (p. 357), tellurium dissolves in sulphuric acid giving a red solution which probably contains a tellurium-sulphur sesquioxide.

The compound is obtainable in the solid state by the addition of powdered tellurium to sulphur trioxide, when combination occurs with evolution of heat. Any excess of sulphur trioxide can be removed mechanically or by evaporation under reduced pressure.⁶

The substance, which is of a type general to the sulphur group (see pp. 6, 338), is a red solid which softens at 30°C . without melting. It is decomposed by water mainly into tellurium and sulphuric acid, whilst in solution in sulphuric acid it undergoes oxidation into basic tellurium sulphate on warming. Between 35° and 90°C . it is stated that the red compound is converted into an isomeric form having a reddish-brown colour.⁷ (See also p. 379.)

Tellurium Sulphates.—By heating a mixture of powdered tellurium and concentrated sulphuric acid until a dry residue remained, Berzelius obtained a white, earthy mass, which after analysis he concluded to be a *disulphate*, $\text{TeO}_2 \cdot 2\text{SO}_3$ or $\text{Te}(\text{SO}_4)_2$.⁸ The composition of the product, however, is somewhat uncertain; on heating it yields a more definite compound of composition $2\text{TeO}_2 \cdot \text{SO}_3$, which can be regarded as a *basic tellurium sulphate* or as a *pyrotelluryl sulphate*. The latter compound

¹ Hageman, *J. Amer. Chem. Soc.*, 1919, 41, 329.

² See also Brauner, *Trans. Chem. Soc.*, 1895, 67, 549; *Zeitsch. anorg. Chem.*, 1902, 32, 378; also Gutbier, *ibid.*, p. 292.

³ Hageman, *loc. cit.*

⁴ Snelling, *J. Amer. Chem. Soc.*, 1912, 34, 802.

⁵ Staudenmaier, *Zeitsch. anorg. Chem.*, 1895, 10, 221.

⁶ Weber, *J. prakt. Chem.*, 1882, [ii.], 25, 218.

⁷ Divers and Shimose, *Ber.*, 1883, 16, 1004, 1884, 17, 858.

⁸ See *Handbook of Chemistry* (Gmelin, 1850), vol. iv., p. 407; also Magnus, *Pogg. Annalen*, 1829, 17, 521.

is also obtained as rhombic crystals ($a : b : c = 0.5265 : 1 : 0.7860$) from a solution of tellurium dioxide in diluted sulphuric acid.¹

Telluropentathionic Acid, $H_2TeS_4O_6$.—The sodium salt of this acid may be prepared by the action of tellurium dioxide on an aqueous solution of sodium thiosulphate in the presence of hydrochloric acid (cf. p. 340):



The salt decomposes in the presence of alkali with separation of tellurium.²

TELLURIUM AND SELENIUM.

Tellurium and selenium are miscible in all proportions when molten, no combination apparently occurring.³

A solution of *tellurium-selenium sesquioxide*, $TeSeO_3$, has been described (p. 357). A *basic tellurium selenate*, $2TeO_2 \cdot SeO_3$, analogous to the foregoing sulphur compound, is obtainable from tellurium oxide and selenic acid.⁴

TELLURIUM AND NITROGEN.

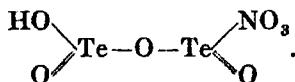
Tellurium Nitride.—The formation of this compound has already been mentioned (see p. 375). It is obtained when anhydrous liquid ammonia reacts in the cold with a tetrahalide of tellurium. It is deep yellow in colour, amorphous, and when dry extremely explosive. Its composition has not been determined with certainty, but its empirical formula is probably TeN or Te_3N_4 .

Tellurium Nitrite.—By the action of nitric acid on tellurium under special conditions, tellurium nitrite may be obtained as a flesh-coloured precipitate. At $100^\circ C$. this precipitate may be dried without decomposition; above this temperature it decomposes with the formation of tellurium dioxide.⁵

Basic Tellurium Nitrate, $Te_2O_3(OH)NO_3$, which has already been mentioned (p. 379), is formed when a solution of tellurium or tellurium dioxide in nitric acid is evaporated without excessive heating.⁶ It crystallises in rhombic pyramidal crystals ($a : b : c = 0.590 : 1 : 0.607$).⁷

When heated, the nitrate undergoes decomposition, which commences at $190^\circ C$., the final residue being tellurium dioxide. Hot water rapidly hydrolyses the salt with formation of tellurium dioxide and nitric acid.

The constitution of this salt is probably ⁸



¹ Brauner, *Monatsh.*, 1889, 10, 419; 1891, 12, 34; Urba, *Zeitsch. Kryst. Min.*, 1891, 19, 5. For complex organic bisulphate compounds containing tellurium, see Drew, *J. Chem. Soc.*, 1926, p. 3054.

² Norris, *J. Amer. Chem. Soc.*, 1906, 28, 1675.

³ Pellini and Vio, *Atti R. Accad. Lincei*, 1906, [v.], 15, ii, 46; Kimata, *Mem. Coll. Sci. Kyōto*, 1915, 1, 119.

⁴ Metzner, *Ann. Chim. Phys.*, 1898, [vii.], 15, 203.

⁵ Oefele, *Pharm. Zentr.-h.*, 1920, 61, 491.

⁶ Klein and Morel, *Bull. Soc. chim.*, 1885, [ii.], 43, 204; Norris, Fay and Edgerly, *Amer. Chem. J.*, 1900, 23, 105; Kothner, *Annalen*, 1901, 319, 1.

⁷ Jaeger, *Proc. K. Akad. Wetensch. Amsterdam*, 1910, 12, 602.

⁸ Klein and Morel, *loc. cit.*

TELLURIUM AND CARBON.

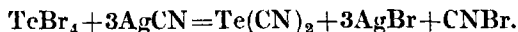
A tellurium analogue of carbon disulphide has not been isolated. A product described as carbon ditelluride¹ has been shown to consist of the sulphidotelluride and its decomposition products.

Carbon Sulphidotelluride, CSt_e.—By passing an arc for some time under carbon disulphide between a graphite cathode and an anode of tellurium containing 10 per cent. of graphite, a reddish-brown solution is obtained which, by repeated fractional extraction with carbon disulphide vapour in a special apparatus, yields a distillate consisting of a dilute solution of carbon sulphidotelluride.² After drying this solution with phosphorus pentoxide and concentrating on a water-bath, using a fractionating column, the pure product may be separated by cooling below -30°C . and protecting from strong light.

Carbon sulphidotelluride forms yellowish-red crystals, melting at -54°C . to a brilliant red liquid of high refractive power. It rapidly decomposes at room temperature. The vapour has a slightly penetrating garlic odour, and when inhaled causes the breath to have a strong garlic odour for a considerable time afterwards. Cryoscopic and ebullioscopic measurements in carbon disulphide and benzene give a molecular weight in agreement with the foregoing formula. The compound is very sensitive towards light, in which decomposition takes place even at -50°C .

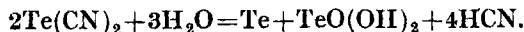
TELLURIUM AND CYANOGEN.

Tellurium Dicyanide, Te(CN)₂.—Tellurium tetrabromide and silver cyanide in a suitable organic solvent such as benzene react according to the equation



The tellurium cyanide may be obtained as a colourless solution on extraction with ether. On evaporation and crystallisation of this solution a double compound of cyanide and ether is obtained, from which the pure cyanide may be prepared by distillation *in vacuo*.

Tellurium dicyanide after a few minutes' exposure to air assumes a graphite-like appearance due to the deposition of tellurium. Water and alkalis hydrolyse it with precipitation of tellurium:



When heated in air the cyanide burns with a pale blue flame. It is soluble to a slight extent in chloroform and carbon tetrachloride. It is also soluble in cold methyl alcohol without change, but when the solution is warmed hydrolysis occurs.

Tellurium dicyanide decomposes into tellurium and cyanogen to a slight extent at 100°C . The decomposition increases more rapidly above this temperature. At about 190°C . there is a sudden increase in the rate of evolution of the gas.³

¹ Stock and Blumenthal, *Ber.*, 1911, 44, 1832.

² Stock and Prætorius, *ibid.*, 1914, 47, 131.

³ Cocksedge, *Trans. Chem. Soc.*, 1908, 93, 2175. For the action of tellurium dicyanide on certain aromatic compounds, see Challenger, Peters and Halévy, *J. Chem. Soc.*, 1926, p. 1648.

NAME INDEX.

- Asmge, 212.
 Abel, 137, 199, 202.
 Abelous, 49.
 Abenius, 158.
 Abersold, 123.
 Abresch, 131.
 Achterberg, 220.
 Ackerman, 123.
 Adam, 150.
 Adams, 298, 354.
 Adhicary, 115.
 Adie, 142, 171, 172.
 Adinolfi, 354.
 Adrianowski, 120.
 Agde, 184.
 Agostini, 65.
 Ahrens, 21.
 Ahrie, 189.
 Aimé, 141.
 Aita, 149.
 d'Albe, 297, 298, 301.
 Alberti, 184.
 Alcock, 66.
 Alexander, 162.
 Alfa, 373.
 Allen, A. H., 172.
 Allen, F. J., 284.
 Allen, J. B., 12, 23, 27, 32.
 Allen, T. B., 178.
 Allin, 356.
 Allison, 36.
 Allmand, 257.
 Almy, 20.
 Aloy, 193, 198.
 Alsterberg, 127.
 Althammer, 175.
 Alvarez, 60.
 Alyea, 132.
 Amadori, 39, 76, 84.
 Amaduzzi, 297, 298.
 Amagat, 106.
 Aminoff, 22.
 Ancel, 293.
 Anderson, E., 123.
 Anderson, R. P., 362, 370, 371.
 Andréef, 112.
 Andreocci, 238.
 Andrews, 171, 172, 178.
 Andrich, 92, 182.
 Anelli, 163.
 Angel, 297.
 Angeletti, 300.
 d'Ans, 137, 144, 173, 175, 181, 189, 190, 191.
 Anschütz, 259.
 Anthon, 166.
 Antony, 54, 55, 206.
 Aoyama, 120.
 Apolant, 374.
 Arbusoff, 135.
 Archibald, 55, 169.
 Arcowski, 255.
 van Arkel, 296.
 Armstrong, H. E., 95, 142, 177, 190, 191.
 Arni, 52, 54, 59.
 Arons, 21, 34.
 Aronstein, 39.
 Artini, 233.
 von Artner, 160.
 Arzaher, 173.
 Arzruni, 21, 173.
 Aschan, 185.
 Ashida, 45.
 Ashley, 201, 223, 372.
 Aslander, 173.
 van Assche, 299.
 Aston, 41, 163, 176, 304, 360, 363.
 Aten, 17, 26, 76, 81, 82, 84.
 Atkinson, 178.
 Atsuki, 164.
 Atynaki, 314.
 van Aubel, 297.
 Auerbach, R., 29, 31, 290, 355, 357.
 Anger, 87, 179.
 Auld, 37, 67, 72.
 Aulich, 335-337.
 Austell, 67.
 Austen, 57.
 Austin, 184, 186.
 Autenrieth, 204.
 d'Avallon, 25.
 Awbery, 33.
 Ayers, 39.
 BAAT, DE, 209.
 Bach, 65 190.
 Bäckstrom, 132.
 Bacon, 49.
 Baedeker, 107.
 Baeyer, 93, 170, 183, 184, 189-191.
 Bagster, 58, 113.
 Bahr, 45, 107.
 Baierlacher, 121.
 Bailey, G. H., 150.
 Bailey, K. C., 282, 283.
 Bailey, R. A., 107, 125.
 Bailey, T. L., 155.
 Bailey, —, 43.
 Bailleul, 180.
 Bain, 44.
 Baines, 200.
 Baissac, 123.

- Baker, H. B., 115, 141, 198, 210, 261, 225,
 331, 337, 352, 360, 362, 363, 371.
 Baker, M., 141.
 Balareff, 178.
 Balduzzi, 319.
 Baly, 107, 125.
 Bamberger, 171, 189-191.
 Bangham, 111.
 Barbaglia, 134.
 Barbieri, 67, 184.
 Barham, 129.
 Barilari, 25.
 Barker, 121, 166.
 Barnes, 39, 165.
 Barre, 174.
 Barreswil, 137.
 Barrow, 91.
 Barruel, 172.
 Barry, 31.
 Barsch, 133.
 von Bartal, 304, 344.
 Barth, 135, 151.
 Bartoli, 107.
 Bartsch, 66.
 Baskerville, 172.
 Bassett, H., 102, 124, 125, 171, 195-199,
 207, 231.
 Bassett, H. P., 61.
 Baubigny, 134, 208, 223.
 Baudrimont, 255, 317, 318, 342.
 Bauer, 57, 66, 106, 115, 124, 299, 308, 363,
 364.
 Baum, 147.
 Baumann, 228.
 Baume, 52, 54, 58, 106, 119, 120, 123.
 Baumgarten, 94.
 Baumstark, 98, 100.
 Bauser, 316.
 Bauzil, 178.
 Bayer, 60.
 Bayer & Co., 9, 87, 126, 182.
 Bayley, 172.
 Bazlen, 131, 226-228, 230.
 Beach, 114.
 Beato, 193.
 Béchamp, 62.
 Becker, F., 229, 351, 352, 357, 359, 381,
 384.
 Becker, H., 114, 136.
 Becker, W., 312.
 Beckmann, E., 17-19, 35, 39, 77, 78, 81-84,
 92, 93, 138, 164, 260, 290, 305, 316-318,
 378.
 Beckurtz, 98, 99.
 Becquerel, 21, 49, 164, 299.
 Bedford, 13.
 Béhal, 87.
 Behrend, 92, 98, 99.
 Beierle, 8.
 Beijerinck, 40.
 Beilstein, 279.
 Bein, 163, 165, 168.
 Beketoff, 55.
 Beljankin, 353.
 Bellati, 296, 297.
 Bellucci, 100, 186.
 Bender, 103, 136, 272.
 Benedikt, 171.
 Benesch, 307.
 Benger, 7, 334, 335, 386.
 Benker, 152.
 Bennett, A. H., 352, 360, 362, 363, 371.
 Bennett, G. M., 40, 126.
 Bérard, 110.
 Beretta, 178.
 Berg, 115, 126, 310, 366, 381, 386, 388.
 Berger, 298.
 Berghoff, 22.
 Berghund, 244, 245.
 Bergmann, 80, 351.
 Bergstrom, 112, 234, 315, 348.
 Berguis, 173.
 Berl, 60, 66, 136, 154, 161, 248, 252.
 Berndt, 298, 299.
 Bernhard, 135.
 Bernthsen, 131, 225, 227, 229, 230.
 Berry, 40.
 Bert, 92.
 Berthelot, 16, 18, 25-28, 35, 55, 58, 61, 63,
 74, 105-107, 109, 114-116, 124, 128,
 131, 139, 141, 142, 148, 165, 168-172,
 180-182, 187, 189, 194, 198-201, 208,
 212, 215, 218, 226, 261, 270, 296, 313,
 318, 370, 371.
 Berthier, 119, 207, 351.
 Berthollet, 48, 139.
 Berthoud, 138, 139, 141.
 Bertrand, 183.
 Berzelius, 3, 42, 254, 262, 278, 286-288,
 299, 303, 312, 347, 351, 358, 361, 373,
 377-380, 382-384.
 Bosson, 77, 79, 88, 90, 91, 96, 97, 100, 131,
 205.
 Bettel, 360.
 Bettendorff, 338.
 Bevan, 191.
 Bhat, 80.
 Bhattacharyya, 35.
 Bianchi, 178.
 Bichowsky, 26, 116, 193.
 Bicskei, 130.
 Bidwell, 32, 297, 299.
 Biehringer, 224, 249.
 Biesalski, 258.
 Bigelow, 132.
 Buijvoet, 65.
 Billandot, 289.
 Billeter, 224.
 Billitz, 96, 98, 99.
 Billy, 225.
 Biltz, 14, 15, 39, 67, 194, 266, 289, 299,
 363, 375, 376.
 Bineau, 109, 162, 165.
 Binz, 227-230, 232.
 Birckenbach, 345, 346.
 Birge, 36.
 Biron, 164, 167.
 Bittner, 68, 223, 224.
 Bjerregaard, 44.
 Bjerrum, 283.
 Black, 32, 123.
 Bladergroen, 180.

- Blanksma, 72.
 Bleckrode, 52, 54, 107, 112, 113.
 Bleier, 14.
 Blennard, 263.
 Blix, 29.
 Bloch, E., 35, 299, 356.
 Bloch, I., 67, 69-73, 81.
 Bloch, J., 232.
 Bloch, L., 35, 37, 299, 356.
 Block, 297.
 Blois, De, 160.
 Blomstrand, 134, 202, 203, 221.
 Blount, 36.
 Bloxam, 25, 39, 67.
 Blumenthal, 322, 323, 335, 391.
 Blumer, 182.
 Boake, 92, 94.
 Bodenstein, 15, 37, 48, 119, 136, 139, 141, 161, 163, 312.
 Bodländer, 136, 139.
 Bodnár, 37, 72, 206.
 Boedeker, 148.
 Boesken, 81.
 Bogen, 312.
 Boggs, 302.
 von Boguski, 22.
 Böhm, 49.
 Bohr, 164.
 Boillot, 48.
 Bollenbach, 185.
 Boltzmann, 32.
 Bonavia, 209.
 Bond, 114.
 Bong, 50.
 Bongiovanni, 195, 281.
 Bonin, 61.
 Bonner, 130.
 Bordet, 58.
 Borgo, 39, 69, 70.
 Borinski, 95-97, 301, 320, 324, 358, 375.
 Bornstein, 53, 279.
 Borntraeger, 292.
 Borsum, 249.
 Bose, 165.
 Bosshard, 232.
 Bothamley, 75.
 Böttger, 60, 67, 80, 359.
 Bouguet, 80.
 Boulouch, 84.
 Boulzourenco, 330.
 Bourgeois, 207, 209.
 Bourion, 79.
 Boutaric, 202.
 Bouty, 124, 164.
 Bowen, 8, 35, 36.
 Bowers, 361, 362, 380.
 Bowmaker, 307.
 Bozza, 147, 174.
 Bradbury, 384.
 Bradley, 45, 136.
 Bradt, 309, 315.
 Brame, 23, 35.
 Bramley, 282.
 Brandt, 32, 122.
 Braessert, 160.
 Braun, 86, 128.
 Brauner, 352, 357, 360, 361, 363, 365, 367, 376, 377, 380-382, 386, 389, 390.
 Brauns, 22, 23.
 Brautigam, 266.
 Brearley, 12, 23, 27, 32.
 Bredig, 164, 186.
 Bresciani, 57.
 Breteau, 63.
 Brezina, 380.
 Bridgman, 22.
 Briegleb, 298.
 Briggs, 166, 191.
 Briner, 112, 152, 155, 250.
 Brioni, 282.
 Brioux, 37.
 Briscoe, 258, 262, 344.
 Briwul, 178.
 Brjuchonensko, 39.
 Brochet, 172.
 Brockmoller, 15, 289.
 Brodie, 16, 19, 20, 28.
 Brönsted, 163.
 Brosche, 131.
 Brotherton, 232.
 Brown, F. C., 297.
 Brown, G. V., 286.
 Brown, O. W., 337.
 Browne, 32, 275, 276.
 Browning, 308, 352, 360, 366, 367, 370, 382-384.
 Brownlee, 27.
 Brückner, 38, 103, 142, 175.
 Brügelmann, 201.
 Brugnattelli, 37, 218.
 Bruhat, 261.
 Bruhl, 121.
 Bruhns, 25, 232.
 Brukl, 365.
 Brunck, 66, 227, 329, 383.
 Brunel, 109, 187.
 Bruner, 5, 61, 371.
 Brunhes, 15, 20.
 Bruni, 69, 70, 76.
 Brünning, 228, 250.
 Brunner, 73.
 Bruylants, 362, 363, 371.
 Bruyn, de, 30.
 Buchanan, 202, 203.
 Buchbock, 272.
 Bucherer, 133, 227.
 Buchholz, 224, 278.
 Buchner, 158, 257.
 Budde, 14.
 Budnikov, 61, 79, 159, 175.
 Buff, 114, 136.
 Bugge, 73.
 Buignet, 129, 207.
 Bungartz, 35.
 Bunsen, 21, 52, 124, 305.
 Bunte, 203, 209.
 Buogo, 10.
 Burch, 171.
 Burgess, 35, 360.
 Burggraff, 111.
 Burghardt, 47.
 Burke, 139, 317, 318, 327.

- Burns, 10, 328.
 Burrell, 112.
 Burrows, 274.
 Burt, B. C., 166.
 Burt, F. P., 42, 111, 233.
 Burton, 123.
 Bush, 152, 171, 304, 359, 372.
 Bushong, 100.
 Busz, 21.
 Butler, 71, 328.

 CADDICK, 257.
 Cady, 113.
 Cailliet, 58, 106, 112, 113.
 Calcagni, 37, 174.
 Callendar, 35.
 Calvert, 121, 171, 172.
 Calzolari, 184, 216, 221, 223.
 Cambi, 147, 174, 201.
 Cameron, C. A., 163, 321, 326-328, 334, 335, 346, 347, 357.
 Cameron, W. H. B., 35.
 Campbell, 122.
 Canneri, 199.
 Cant, 107.
 Capelle, 19, 34, 258.
 Capstick, 52.
 Cardoso, 52, 54, 59, 112, 113
 Carey, 131.
 Carius, 44, 53, 76, 78-81, 87, 88, 91, 108, 109, 124.
 Carli, de, 113, 120.
 Carnelley, 32, 35, 296, 297, 354, 377.
 Caro, 65, 170, 186, 187, 189, 191, 192.
 Carobbi, 174.
 Carpenter, 153, 164, 206, 207, 209.
 Carpini, 297.
 Carpmael, 261.
 Carrara, 40, 93.
 Carson, 16-18, 21, 84, 116, 174, 220, 223.
 Carter, 116, 118, 119, 328.
 Carvallo, 113.
 Casalino, 139.
 Casamajor, 63.
 Casolari, 205.
 Cassella, 80.
 Causse, 225, 226.
 Cauwood, 307.
 Centner, 216, 219.
 Centnerszwer, 73, 112-114.
 Cernatescu, 283.
 Cesaro, 350.
 Chabrié, 317, 326, 328, 331.
 Chakravarti, 80.
 Challenger, 273, 277, 391.
 Chamberlin, 56.
 Chance, 197, 211, 213-217, 260, 262, 264.
 Chapin, 37, 215.
 Chappuis, 35, 110.
 Chargaiff, 276.
 Charlton, 123.
 Chattaway, 284.
 Chatterjee, 177.
 Chaudron, 66.
 Chaussier, 192.
 Chauveau, 60.

 Chauvenet, 202, 291, 329, 333.
 Chavastelon, 35.
 Chevrier, 48, 78, 81.
 Chikashigé, 358, 363.
 Chlopin, 300, 358.
 Cholodny, 290, 292.
 Chowrenko, 49.
 Chrétien, 299.
 Christiansen, 222, 228, 232.
 Ciochina, 45.
 van Cittert, 178.
 Claesson, 100.
 Clarens, 282.
 Clark, 44, 122, 159, 185, 329.
 Clarke, 8, 56, 113, 348, 380, 383, 385.
 Classen, 57, 66, 224.
 Claubry, de, 78, 248.
 Claus, 242, 245-247, 317, 319, 323, 340, 341.
 Clausnizer, 97, 99, 142, 324, 326, 328.
 Clément, 247.
 Clemons, 308.
 Clerici, 201.
 Clermont, de, 62.
 Clever, 235, 236, 240.
 Clews, 116, 118.
 Cloëz, 25, 26, 49, 262, 338.
 Cluzel, 55.
 Cockledge, 377, 391.
 Coehn, 114, 136.
 Coffey, 80.
 Cohen, 23, 353.
 Colefax, 193, 198, 211, 216, 221.
 Coleman, 152, 155, 156.
 Coh, 319.
 Collet, 354.
 Colson, 173, 193, 196.
 Colt, 30.
 Colvert-Glauert, 124.
 Coninck, de, 258, 291, 327-329, 333, 338.
 Conover, 89, 90.
 Conroy, 172.
 Cooke, 42, 61, 170.
 Cookson, 172.
 Cooley, 356.
 Coppadoro, 164.
 Coppetti, 130.
 Coppola, 112.
 Corbin, 45, 136.
 Cornec, 330.
 Cornog, 103, 136.
 Correnwinder, 48, 49.
 Cory, 158.
 Cossa, 22, 48, 261.
 Costa, 40, 81.
 Coste, 292, 363.
 Costeanu, 57.
 Cousins, 16.
 Coustal, 61, 63.
 Cox, 315, 316, 320.
 Craig, 66, 129.
 Crane, 352.
 Craven, 45.
 Crawford, 45.
 Crespi, 111.
 Crompton, 168.

- Crocker, 343-348.
 Cross, 27, 35, 123, 191, 357.
 Crotogino, 172.
 Croullebois, 52.
 Cumming, 56, 149, 156.
 Cundall, 11, 172.
 Cupe, 109, 110, 164.
 Curjel, 175.
 Carrier, 275.
 Curtis, 328.
 Curtius, 218, 253.
 Curtman, 283.
 Cushman, 166.
 Casmano, 92.
 Cuthbertson, 35, 52, 107, 299.
 Czapek, 302.
 Czernotzky, 198, 199, 217, 219.

 Daquin, 33.
 Dakin, 185.
 Dalton, 220.
 Dalziel, 81.
 Damons, 353, 374, 376, 378, 379.
 Dammer, 172.
 Damoiseau, 39.
 Dana, 21, 350.
 Danneel, 38, 61, 91.
 Dannenberg, 19.
 Dargan, 103, 136.
 Darzens, 91.
 Datta, 297.
 Davey, 65.
 Davidson, 174.
 Davis, 166, 168, 235.
 Davy, 246, 335, 346, 347.
 Dawkins, 174.
 Day, 35, 45.
 Dean, 58, 66, 179, 359.
 De Blois, 160.
 Debray, 25, 286.
 Debraye, 49.
 Debucquet, 123.
 Debus, 28, 119, 193, 198, 206, 210-212, 214, 215, 217-219, 222, 274.
 Dechant, 54.
 Dede, 61.
 Dehnel, 228.
 Delaplace, 39.
 Delépine, 35, 40, 172.
 Delfs, 61, 119.
 Del Fresno, 232.
 Del Regno, 297, 298.
 Del Rio, 286.
 Demarçay, 238-240.
 Demarcel, 126.
 Demarteau, 67.
 Denham, 50, 80, 91.
 Denigès, 177, 263, 305, 336, 387.
 Denis, 179.
 Dennis, 287, 326, 328, 332, 336, 337, 362, 364, 370, 371.
 Desmet, 362.
 Désormes, 247.
 Despretz, 34.
 Deville, 14, 16, 20, 21, 23, 25, 27, 34, 56, 114, 136, 289, 354.

 Devine, 45.
 Dewar, 35, 54, 107, 255.
 Dezani, 278.
 Dhar, 82.
 Diacon, 197, 211, 218-217.
 Diénert, 201.
 von Dienes, 69.
 Diestelmeier, 15, 299, 356.
 Dieterici, 165, 166.
 Dietzel, 124, 125.
 Dietzenbacher, 29.
 Dikova, 188.
 Dimitrow, 66, 205.
 Dittmar, 293.
 Ditte, 143, 171, 313, 320, 321, 325, 327, 352, 353, 356, 377, 381.
 Dittler, 8, 31, 66.
 Dittmar, 162.
 Dittrich, 185.
 Ditz, 174.
 Divers, 8, 39, 50, 58, 120, 126, 134, 137, 143, 155, 193, 224, 243-246, 251-253, 289, 316, 328, 338, 350, 357, 370, 379, 389.
 Dixon, 134, 261, 279.
 Dobbie, 15, 305, 355.
 Doctor, 312-314.
 Dodd, 299.
 Dodgson, 171.
 Dodonov, 71.
 Domanicki, 79.
 Domergue, 27.
 Domeyko, 350.
 Dominik, 173.
 Domke, 163, 165, 168.
 Donath, 40, 60, 128, 193, 365, 381.
 Doolan, 224, 355, 356, 379.
 Dopping, 38, 109.
 Doran, 263.
 Doroshevski, 136.
 van Dorp, 173.
 Dougherty, 44.
 Doughty, 333.
 Drakeley, 49, 63.
 Draper, 50, 291, 292.
 von Drathen, 245.
 Draves, 37.
 Drechsel, 70, 72, 193, 203.
 Dreifuss, 363.
 Drew, 359, 372, 376, 390.
 Drion, 111, 112.
 Drossbach, 124, 196, 232.
 Drown, 44.
 Druce, 105, 172.
 Drucker, 66, 109, 113, 124, 169.
 Drugman, 34.
 Drummond, 45.
 Dubosc, 283.
 Ducher, 158.
 Dudley, 348, 356, 360-362, 380.
 Duhem, 17, 23, 83.
 Dumas, 3, 42, 56, 80, 303.
 Dunaieva, 129.
 Dunez, 45.
 Dunn, 110.
 Dunnicliff, 58.

- Dunningham, 133, 193, 195.
 Dunsby, 159.
 Dunstan, 145, 168.
 Durand, 282, 283.
 Durgart, 351.
 Durham, 62.
 Dürkes, 178.
 Durrans, 92, 94.
 Durrant, 102, 116, 117, 124, 125, 171, 195-199, 231.
 Dušchak, 177.
 Dussy, 15, 17, 20.
 Duter, 32.
 Dutoit, 113, 199.
 Dyer, 45.
 van Dyke, 355.
 Dymond, 129, 207.
 Dyson, 287-289, 301, 351.

 EATON, 45.
 Ebell, 31.
 Ebelmen, 80.
 Ebert, 375, 377.
 van Eck, 258.
 Eckert, 296, 355.
 Eckhardt, 188.
 Eckman, 114.
 Edeleanu, 122.
 Eder, 35, 299.
 Edgerly, 352, 360, 361, 390.
 Edinger, 80.
 Egriwe, 122, 129.
 Egerton, 62.
 Eggeling, 199.
 Egger, 30.
 Egidius, 102.
 Egleston, 350.
 Eigenberger, 45.
 Einecke, 64.
 Ekker, 226.
 Ekmann, 303.
 Elbs, 169, 170, 181, 183, 186.
 Elder, 333.
 Eliasberg, 66, 205.
 Elion, 48.
 Ellingham, 257.
 Elliott, 54, 249.
 Elton, 206.
 Elvins, 376.
 Emeléus, 37, 261.
 Emslander, 181, 294, 295.
 Endemann, 109.
 Endo, 354, 363.
 Engel, 26.
 Engelmann, 25.
 Engeroff, 295, 307.
 Englert, 229.
 Enklaar, 169.
 Entat, 179.
 Ephraim, 84, 91, 94, 99, 120, 142, 175, 241, 243, 253, 284, 343.
 Ercolini, 184, 185.
 Erdenbrecher, 182.
 Erdmann, 16, 19, 20, 29, 72, 303.
 Ernyei, 370-372.
 Ero, 173.

 Ertl, 371.
 Espenhahn, 66, 198.
 Espenschied, 340, 375.
 Espil, 330.
 Esselmann, 257.
 Essin, 182, 207.
 Etard, 9, 49, 174, 313, 336.
 Euler, 38, 359.
 Eumorfopoulos, 35.
 Evans, B. S., 45.
 Evans, F. P., 318, 320.
 Evans, K., 56.
 Evans, R. B., 372.
 Evershed, 35.
 Eversheim, 124.
 Ewald, 9.
 Exner, 35, 54.
 Eymer, 227.

 FABRE, 292, 313, 314, 337, 353, 354, 370, 371.
 Fahlberg, 37.
 Faktor, 200, 204.
 Falcicola, 205, 376.
 Falcke, 71.
 Faldini, 159.
 Faraday, 53, 114.
 Faragher, 45.
 Farbaky, 351.
 Farr, 18, 25, 34.
 Fatio, 121.
 Fauser, 53.
 Faust, 290.
 Favre, 27, 107, 110, 174.
 Fawsitt, 77, 171.
 Fay, 214, 340, 352, 353, 360, 361, 363, 367, 390.
 Fazi, de, 45, 273.
 Federhn, 185.
 Federow, 128.
 Fehn, 179.
 Fehrenbach, 137.
 Feigensohn, 155.
 Feigl, 64, 65, 199, 204, 205, 276, 283.
 Feit, 201.
 Feld, 63, 206, 215, 218, 223.
 Felipe, 169.
 von Fellenberg, 177.
 Felsing, 107.
 Fenaroli, 31, 356.
 Fenton, 110.
 Fenwick, 66, 308.
 Ferguson, 106, 114, 116, 122, 165, 169.
 Ferrario, 80, 83.
 Féry, 168.
 Fetkenheuer, 268.
 Fetzner, 62.
 Ficai, 111.
 Fichter, 171, 180, 182, 376.
 Fife, 12.
 Filhol, 38, 47, 57.
 Finch, 147.
 Findlay, 196.
 Fink, 119, 136.
 Finkener, 50.
 Fiorentino, 112.

- Firth, 227.
 Fischebeck, 37.
 Fischbeck, 64.
 Fischer, 65, 73, 81, 82, 116, 126, 224, 236, 263, 274, 314, 381.
 Fischer-Treuenfeld, 33.
 Fischler, 151.
 Fisher, 264.
 Fitzgerald, 113.
 Fizeau, 354.
 Flatow, 260.
 Fleck, 200.
 Fleischer, 148, 284.
 Fletcher, 49.
 Flint, 352, 360, 366, 379.
 Floyd, 45, 136.
 Flury, 295, 358, 365, 375, 377, 378, 381, 386.
 Foà, 284.
 Fock, 199, 210.
 Fodor, 32.
 Foerster, 124, 131, 132, 194, 196, 198, 211, 212, 215, 216, 218, 219, 222, 232.
 Fogh, 197, 200, 204.
 Foisik, 362.
 Földes, 13.
 Follansbee, 302.
 Fonzes-Diacon, 50, 54, 61, 299, 312-314, 371.
 Foote, 281.
 Footner, 203.
 Forch, 21, 22.
 Forcrand, de, 54, 58, 59, 120, 312, 313, 371.
 Fordos, 27, 28, 37, 129, 171, 194, 208, 212-215, 217, 219, 239.
 Formhals, 232.
 Forrer, 152.
 Forster, 182.
 Förster, 207.
 Forsyth, 127.
 Foss, 136.
 Fosse, 183.
 Fourcroy, 111.
 Fournier, 55, 77, 79, 88, 360.
 Fowles, 172.
 Fox, 15, 110, 305, 355.
 Fraenkel, 23.
 France, 169.
 Francis, 45, 235.
 Franck, 61.
 Frank, 77.
 Frankland, 273.
 Franklin, 113, 172.
 Fraps, 135.
 Frasch, 10.
 Frazer, 166.
 Freese, 108.
 Frémy, 127, 242, 245, 247, 248.
 Frenkenberg, 198.
 Frericha, 179, 308, 365.
 Fresenius, 47, 50, 65, 177, 305.
 Freundlich, 31, 32, 274, 279.
 Freyer, 56.
 Frick, 323.
 Fridli, 309.
 Friedberger, 182.
 Friedel, 26.
 Friederich, 181, 189-191.
 Friederichs, 374.
 Friedheim, 66, 178.
 Friedländer, 80.
 Friedrich, 38, 174, 299, 300, 336, 375, 376.
 Friend, 123, 131, 184, 188, 190.
 Fries, 101.
 Friessner, 207.
 Friman, 299.
 Frischauer, 34.
 Fritsch, 224, 286.
 Fritsch-Lang, 55.
 Froebel, 292.
 Fröhlich, 38, 61.
 Fromm, 101, 102, 229, 231.
 Frommel, 62.
 Frossard, 228.
 Frühling, 43.
 Fuchs, 78, 105.
 Fukuda, 36.
 Fuller, 51.
 Futagami, 356.
 GABILLON, 179.
 Gaertner, 277.
 Gahl, 194.
 Gaillard, 199.
 Galanos, 124, 125.
 Gallagher, 113.
 Galletly, 49.
 Gallo, 366.
 Ganassini, 281.
 Garard, 30.
 Gardner, 302.
 Garelli, 300.
 von Garn, 307, 329.
 Garnak, 287.
 Garner, 273.
 Garnier, 166.
 Garrett, 107, 124.
 Garrigou, 47.
 Garrison, 364.
 Gasparini, 44.
 Gassmann, 286.
 Gaubert, 17, 26, 33.
 Gaudechon, 114.
 Gautier, 47, 50, 52, 57, 60, 63, 270.
 Gavelle, 145.
 Gay-Lussac, 50, 84, 148, 152, 178, 192, 206, 208, 248.
 Gebauer-Fulnegg, 44.
 Geib, 290.
 Geipel, 354.
 Geisel, 29, 38, 39, 82, 194, 211, 234-237.
 Gertner, 49.
 Gélis, 27, 28, 37, 49, 129, 171, 194, 206, 208, 212-215, 217, 219, 239, 269.
 Georgiewski, 32.
 von Gerichten, 337.
 Germuth, 179.
 Gernez, 15, 17, 20, 23-25, 33, 36, 83, 299, 316, 327, 374.
 Getman, 107, 125.
 Genther, 57, 98, 109, 131, 142, 169, 177, 200, 279.

- Ghosh, 32, 123.
 Glachery, 79.
 Gibbs, 112.
 Gies, 359.
 Gil, 193.
 Gilbert, 369, 372.
 Gilchrist, 150.
 Giles, 108, 124.
 Gilfillan, 274.
 Gill, 109, 113.
 Giller, 31.
 Gilles, 35, 36.
 Gillson, 353.
 Gilson, 316.
 Giran, 103, 140, 167, 180.
 Girard, 49, 248, 265.
 Gladstone, 40, 169, 334.
 Glaser, 201.
 Glassett, 185.
 Glauser, 324, 381.
 Gloss, 24, 39.
 Glover, 150, 172, 287, 288.
 Glütz, 285.
 Godby, 135.
 Goddard, 372.
 Goebel, 162, 276.
 Goetz, 23.
 Goldbach, 224.
 Goldberg, 80, 264.
 Goldschmidt, 63.
 Goldstein, 369.
 Golla, 76, 80.
 Gonder, 77.
 González, 269.
 Gooch, 308, 329, 334, 335, 363, 367, 377,
 381, 382, 386.
 Gordon, 32.
 Gortner, 179.
 Gosio, 330, 360.
 Gossner, 385.
 Goswami, 133.
 Graf, 35, 91.
 Graham, 15, 36, 80, 233, 238, 336.
 Graire, 130, 153.
 Gramont, de, 35, 36, 299, 356.
 Grandmougin, 226.
 Grassi, 109.
 Grassner, 45.
 Gray, 13.
 Groathouse, 169.
 Green, 91, 183, 184.
 Greenbaum, 388.
 Greenewalt, 166.
 Greer, 226, 229.
 Greider, 111.
 Griffet, 27.
 Griffin, 45.
 Griffiths, 35, 297.
 Grignard, 91, 96, 97.
 van der Grinton, 296.
 Gripon, 49, 218.
 Grob, 232.
 Groeneveld, 37.
 Grollman, 166.
 Grounds, 152.
 Grove, 121.
 Gruener, 35.
 Grünert, E., 116.
 Grunert, H., 174.
 Grünhut, 121.
 Grünsteidl, 43.
 Grunthal, 204, 224.
 Grunwald, 356.
 Grzenkowski, 110.
 Guareschi, 29, 37, 60, 67.
 Gudden, 297, 298.
 Guénot, 360.
 Guerasimov, 32.
 Guerbert, 37.
 Guérout, 81, 126.
 Guerout, 226.
 Guglielmo, 39.
 Guichard, 286.
 Guilleminot, 297.
 Guinet, 262.
 Guttonneau, 13, 194.
 Gulbins, 341.
 Gunder, 44.
 Guntz, 114.
 Gurewitsch, 91, 99, 241.
 Gustavson, 92, 95.
 Gutbier, 31, 293-296, 307, 319, 329, 338,
 355-358, 362, 365-367, 370, 375, 377,
 378, 380, 381, 384-386, 389.
 Guthrie, 80, 84.
 Gutmann, 101, 203, 205, 215, 222.
 Guyot, 300.
 Guze, 112.
 Gyr, 113.
 HAASE, 178.
 Haber, 178, 182.
 Habermann, 8, 50, 60.
 Hac, 133.
 Hackl, 45, 61, 204.
 Haeberle, 388.
 Haga, 244-247, 251, 253, 328.
 Hageman, 89, 389.
 Hagglund, 132, 133.
 Hahn, 177, 199, 312, 330, 342.
 Haken, 354.
 Hale, 359.
 Halévy, 391.
 Hall, R. D., 79, 300.
 Hall, W. T., 44.
 Haller, 122.
 Hallwachs, 168.
 Hamburger, 178.
 Hammick, 16, 17, 76, 120.
 Hamner, 15.
 Hampe, 50.
 Hamprecht, 132.
 Hansi, 45.
 Hänisch, 111, 116.
 Hannay, 83, 113, 259, 351.
 Hansen, 359.
 Hanslian, 39, 84, 290, 378.
 Hantzsck, 94, 163, 164, 241, 242, 246, 251,
 284.
 Hanuš, 200.
 Harcourt, 352, 360.
 Harding, 263.

- Hardingham, 104.
 Hargreaves, 133, 193, 195.
 Harpf, 111.
 Harrington, 47.
 Harris, 283.
 Hart, 105, 116, 150.
 Hartley, 35, 164, 356.
 Hartmann, 50, 152.
 Hartog, 100.
 Harvey, 77, 79, 152.
 Haschek, 35.
 Hasenbaumer, 121.
 Hasenclever, 171.
 Hassel, 185.
 Haasreidter, 66.
 Hatton, 121.
 Haustenain, 191, 192.
 von Hauer, 361, 377.
 Hauser, 45.
 Hautefeuille, 27, 49, 79.
 Hawes, 66.
 Hayes, 159.
 Haywood, 37.
 Heaps, 297.
 Heberlein, 37, 67, 72, 104.
 Hecht, 21, 38, 237.
 Heeren, 210.
 Hegel, 263.
 von der Heide-Melzer, 45.
 Heider, 332, 336.
 Hein, 45.
 Heinrich, 45, 294.
 Heinrichs, 66.
 Heinze, 128.
 Helff, 39.
 Hell, 273.
 Heller, 203.
 Helwig, 232.
 Hempel, 44, 103, 136, 153, 155, 270, 271,
 312, 370.
 Hempelmann, 115.
 Henderson, 119.
 Hendrixson, 130.
 Hengl, 13.
 Henglein, 110.
 Henkel, 180.
 Henning, 112.
 Henri, 36.
 Henriques, 80.
 Henry, 63, 84.
 Henville, 123.
 Herold, 84.
 Herrent, 113.
 Hertlein, 40, 198, 201, 208-210, 213-216,
 218-221.
 Hertz, 39.
 Herz, 261.
 Heschus, 32, 298.
 Hess, 136.
 Heumann, 37, 88, 89, 92, 96-99.
 Heureuse, d', 142.
 Hewitt, 80, 201.
 Heycock, 82.
 Meyer, 104.
 Heyl, 226, 229.
 Heymann, 153.
 Heyn, 115, 299, 363.
 Hibbert, 188, 334.
 Hicks, 79.
 Higgin, 27, 35, 357.
 Higgins, 33, 261.
 Higson, 184, 185, 227.
 Hildebrand, 39.
 Hilditch, 40.
 Hill, 36, 90, 114, 137, 144.
 Hilpert, 124.
 Himly, 202.
 Himmelbauer, 31.
 Hinrichsen, 364.
 Hinsberg, 327, 328, 345.
 Hinschelwood, 93.
 Hurd, 121.
 Hirose, 387.
 Hirst, 179.
 Hittori, 35, 292, 299.
 Hlasko, de, 371.
 Höchtlen, 267.
 Hock, 40.
 Hodgkinson, 121.
 Hoel, 275, 276.
 Hoerenz, 86.
 Hoffman, W. F., 179.
 Hoffmann, E., 133.
 Hoffmann, F., 16.
 Hoffmann, G. F., 325, 326.
 Hoffmann, H., 170.
 Hoffmann, J., 29, 305, 313, 349.
 Hoffmann, K., 258.
 Hoffmann, R., 276, 277.
 Hofman, 175.
 Hofmann, A. W., 68, 114, 115, 136, 261,
 270, 280, 284.
 Hofmann, K. A., 267.
 Hofmeier, 333.
 Hogbom, 373.
 Hohn, 67, 69-73.
 Holborn, 259.
 Holl, 241, 242.
 Hollandt, 179.
 Holland, 173.
 Holleman, 194, 196, 198.
 Holluta, 201.
 Holmberg, 72, 80, 267.
 Holmes, 15, 16, 18, 21, 28, 173, 298.
 Holst, 52.
 Holtz, 256.
 Holweck, 36.
 Homberger, 365.
 Homma, 60.
 Honda, 354.
 Hönig, 201, 208, 211.
 Hoover, 42.
 Hopfield, 36.
 Hopkins, 302, 360.
 Hornig, 212, 213, 218.
 Horsch, 57, 60.
 von Horvath, 358, 374.
 Hovorka, 200.
 Howard, 120.
 Howden, 178.
 Howe, 15.
 Howland, 363, 381, 382, 386.

Howlett, 35.
 Hoyer, 43.
 Hradecky, 335.
 Huber, 296, 355, 365.
 Hübner, 81.
 Hudson, 108, 110.
 Hærræ, 28.
 Huff, 255, 256, 263, 332.
 Hugget, 109, 113.
 Huggins, 65.
 Hughes, 59, 129, 207.
 Hugot, 67, 289, 300.
 Hulett, 177, 254.
 Hulot, 351, 366, 388.
 Hampert, 180, 182.
 Humphreys, 299.
 Hunt, 9.
 Hunter, 281.
 Huntington, 104.
 Häppner, 152.
 Hurst, 123.
 Hurter, 131.
 Hutchins, 386, 387.
 Hutin, 66, 104.
 Hüttner, 45.
 Huybrechts, 169.

Iles, 37.
 Ilsovay, 20.
 Imray, 13.
 Inghilleri, 262.
 Ingls, 153, 186.
 Ingram, 35.
 Isaac, 228.
 Isaacs, 44.
 Isambert, 81.
 Ishikawa, 80.
 van Iterson, 19.
 Ivanoff, 205, 308, 330.
 Iwase, 30.
 Izard, 329.

JABŁOŃSKI, 196, 198, 199.
 Jackson, 315.
 Jacob, 185.
 Jacobi, 121.
 Jacobsen, 37, 52.
 Jacquelin, 207, 245.
 Jacques, 200.
 Jaeger, 38, 162, 358, 378, 390.
 Jahn, 169.
 James, 49, 119, 328.
 Jamieson, 205, 223.
 Jander, 179, 385, 387.
 Jannasch, 329.
 Jannek, 307, 326, 329.
 Januario, 48.
 Jaquerod, 41, 106.
 Järvinen, 45, 66.
 Jay, 253.
 Jayson, 66.
 Jellinek, 38, 47, 59, 124, 226-228, 230-232.
 Jenks, 39.
 Jensen, 178.
 Jilek, 366.
 Joachimoglu, 387.
 VOL. VII. : II.

Joannes, 279.
 Joffe, 13.
 Johansen, 56.
 Jöhlén, 32.
 Johnson, 35, 159, 171, 172, 229, 354.
 Johnston, 49.
 Jones, C. O., 337.
 Jones, C. W. H., 248, 250, 251.
 Jones, E. V., 356, 360, 362.
 Jones, F., 34, 39, 170.
 Jones, F. B., 263.
 Jones, G., 42.
 Jones, G. G., 74.
 Jones, H. C., 20, 30, 67, 72, 168, 169, 193.
 Jones, H. O., 123, 255.
 Jones, J. S., 13.
 Jones, L. M., 339.
 Jorissen, 37, 38.
 Josephy, 215, 218, 224.
 Joubert, 37.
 Jouniaux, 355.
 Judd, 27.
 Juge-Boirard, 66.
 Juhen, 321.
 Jungfleisch, 109.
 KAHAN, 266, 267.
 Kahane, 44, 45.
 Kahlbaum, 352, 353.
 Kailan, 184.
 van der Kam, 254.
 Kangro, 92.
 Kanhauser, 174.
 Kannonnikoff, 40.
 Kao, 316, 317, 366.
 Kapff, 226.
 Karaoglanow, 66, 178.
 Karl, 142.
 Karo, 37.
 Karrer, 286.
 Karssen, 65.
 Kás, 303.
 Kasarnovskii, 298.
 Kasarnowsky, 359, 362.
 Kastle, 19, 103, 184, 279.
 Kastner, 66, 365.
 Katayama, 163.
 Kato, 169, 177.
 Kaufmann, 212, 213, 215, 216, 218, 219, 277, 345, 346, 348.
 Kaveler, 260.
 Kay, 169.
 Kaye, 33.
 Kayser, 38, 110.
 Keane, 44.
 Kehren, 179.
 Kellas, 16, 17, 19, 34.
 Keller, 30, 352.
 Kellermann, 345, 346.
 Kellett, 376.
 Kelley, 19.
 Kelly, 39.
 Kemp, 70.
 Kemper, 57.
 Kempf, 186, 188.
 Kendall, 164, 174.

- Kendrick, 151.
 Kennedy, 45.
 Keppeler, 119, 137, 144, 161, 175.
 Kermann, 86.
 Kerp, 124.
 Kerschbaum, 164, 198, 199.
 Kershaw, 160.
 Kerstein, 276, 277.
 Kersten, 286.
 Kessel, 57.
 Kessler, 212, 217, 218.
 Kestner, 150.
 Kettner, 281.
 Keyes, 259.
 Kilpatrick, 199.
 Kimata, 300, 358, 363, 390.
 Kimura, 299, 356, 363.
 King, A. T., 179, 200, 204.
 King, C. V., 184, 186.
 Kionka, 121.
 Kipp, 51.
 Kirkpatrick, 385.
 Kirscher, 60.
 Kirschner, 283.
 von Kiss, 185.
 Kitaibel, 351.
 Kitajima, 45.
 Klages, 327.
 Klaproth, 351.
 Klar, 45.
 Klason, 80, 270, 272, 273, 280, 284, 309, 310.
 Klein, 43, 115, 353, 379-381, 390.
 Klemenc, 182.
 Klemenčić, 107.
 Kling, 45.
 Klinger, 39.
 Klooster, 38.
 Klosky, 111.
 Klüss, 199, 210.
 Knapp, 20, 30, 123.
 Knecht, 188, 226.
 Knietach, 138, 141, 145, 146, 159, 160, 162, 165, 167, 168, 171, 172.
 Knoll, 95.
 Knox, 62.
 Kobayashi, 363.
 Kobbé, 13.
 Koch, 242, 245, 287, 293, 355.
 Köchlin, 88, 89, 92, 97-99.
 Koelsch, 66.
 Koenigsberger, 299.
 Kögler, 345, 346, 348.
 Köhler, 33, 57, 293.
 Kohlrausch, 163-165, 168.
 Kohlschütter, 25.
 Kohn, 14, 79, 177.
 Kohout, 45, 136.
 Kokscharow, 21.
 Kolb, 110, 165.
 Kolbe, 59, 171, 208, 272, 365.
 Kolkmeijer, 65.
 Koller, 287, 326, 328, 332, 336, 337, 364.
 Kolthoff, 47, 129, 130, 169, 177, 178, 198, 199, 201, 215.
 Komarovsky, 64.
 Konarsky, 45.
 Konek, 326.
 König, 121, 155, 252, 280.
 Koninck, de, 44, 61, 201, 205.
 Konowalov, 48, 96, 99.
 Kopp, 21, 34, 40, 48.
 Köppen, 136, 139.
 Koppers, 11.
 Koref, 256.
 Korinth, 26.
 Kornblum, 120.
 Korndörfer, 83.
 Korsakov, 45.
 Kőszegi, 178.
 Köthner, 352, 361, 384, 390.
 Kozlov, 169.
 Kraft, 34, 153, 163, 296, 327, 333, 334, 352, 354.
 Krak, 301.
 Kramer, 9.
 Kranendieck, 141.
 Kraus, 9, 172, 354.
 Krause, 328, 330.
 Kraut, 210.
 Krebs, 57, 62.
 Krehlk, 304.
 Kremann, 164, 169, 300, 333.
 Kretov, 77, 80, 82.
 Krige, 109, 123.
 Kröhnert, 128.
 Kröner, 353.
 Kruemmer, 9.
 Krügel, 54.
 Kruger, 174.
 Krüger, 39.
 Kruss, 282.
 Krutwig, 120.
 van 't Kruijs, 177.
 Kruyt, 16, 18, 21, 22, 25, 296, 298.
 Krylow, 182.
 Kubel, 131.
 Kubierschky, 201.
 Kubisch, 131, 132.
 Kubota, 45.
 Kudoh, 161.
 Kühl, 45.
 Kuhlmann, 227.
 Kuhne, 155.
 Kulka, 60.
 Künzer, 35, 39.
 Küpferer, 299.
 Kurbatoff, 21, 41.
 Kurrelmeyer, 32.
 Kurtenacker, 68, 130, 179, 198, 199, 205, 212, 213, 215-219, 223, 224.
 Kuss, 112, 270.
 Küster, 16, 20, 37, 67, 72, 136, 161, 177.
 Kuzma, 304, 365.
 Kyropoulos, 299.
 LABES, 302, 359.
 Laoroute, 35, 356.
 Ladenburg, 54.
 Lallemant, 18.
 Lamb, 318.
 Lamers, 84.

- Lampadius**, 255.
Landmann, 331.
Landolt, 53, 127, 198, 279.
Landon, 174.
Lane, 45.
Lang, 116, 178, 220, 223, 356.
Lange, 111, 112, 114, 115, 124, 128, 196, 232.
Langer, 55, 106.
Langford, 16.
Langlois, 210, 212.
Langner, 326.
Lapicque, 331.
Larhardt, 228.
Lassaigne, 38, 347.
Lassieur, 45.
Lathey, 170.
Lauste, 301.
Lea, 200.
Lebeau, 39, 73, 74, 84, 85, 86, 315, 326.
Le Blanc, 92, 139, 140, 168, 188, 300, 358, 359.
Le Chatelier, 291, 296.
Leche, 179.
Lecher, 276, 278.
Lederer, 359, 372, 374.
Leduc, 52, 54, 106.
Leeuw, 16.
Lefebvre, 32.
Lefort, 44.
Legeler, 257.
Legrain, 49.
Lehmann, 25, 60, 121.
Leisek, 184.
Lemery, 135.
Lenard, 63.
Lengyl, 255.
Lenher, 90, 94, 300, 301, 303, 316, 317, 321-327, 334, 340, 341, 352, 354, 358-360, 362, 365-367, 374-377, 380-384.
Lepage, 57.
Lepin, 96.
Leroux, 38, 299.
Le Roux, 63.
Lesure, 45.
Levaditi, 355, 360.
Levi, 159, 182-185, 194, 196, 214, 265.
Levol, 178.
Levy, 279.
Lewes, 215, 216, 219.
Lewis, 16, 33, 116, 131, 160.
Leysaht, 45.
Lichty, 138-140, 164.
Lidow, 49.
Liebermann, 263.
Liebig, 47, 67, 68.
Liepe, 277.
Liesche, 17, 35.
Liesegang, 32.
Lifschitz, 32.
Linde, 106.
Linder, 61, 63, 153.
Lindh, 36.
Lindner, 108, 124, 374.
Linebarger, 84, 174.
Linnemann, 277, 345.
Lipman, 13.
Lippmann, 80.
Littman, 308.
Littmann, 155.
Liveing, 107, 350.
Livingston, 166.
Lloyd, 121.
Locke, 67.
Lockyer, 8, 299.
Loevenhart, 184.
Loew, 124, 245, 281.
Loewenherz, 186, 187.
Logan, 301.
Lohmann, 329, 338.
Loir, 111.
Londro, de, 350.
Longi, 201, 209.
Loomis, 165.
Lora, 30.
Lorand, 80.
Lorber, 179.
Lorenz, 59, 62.
Losana, 4, 45.
Lossen, 294.
Lott, 173.
Low, 254, 255.
Lowe, 351, 357.
Lowery, 260.
Lowry, 74, 75, 189, 191, 254, 369, 372.
Lubarski, 188.
Luca, de, 27, 148.
Lucas, 45, 136, 356.
Luchini, 199.
Luerus, 228.
Luckow, 126, 201, 208.
Ludwig, 65, 218.
Luff, 66.
Lukas, 366.
Lukens, 79.
Lumière, 63, 132, 227.
Lumsden, 80.
Lundy, 10.
Lunge, 44, 56, 103, 104, 127, 129, 130, 136, 149, 153-156, 158, 161-163, 165, 172, 201, 214, 248, 250, 252.
Lussana, 296.
Luther, 169.
Luty, 152.
Lyons, 304, 309, 315, 359, 372.
Lyte, 66.
MAASS, 112, 122, 132.
Maassen, 39.
Macagno, 263.
Macallan, 163, 321, 326, 327, 334, 357.
Macaulay, 126, 130.
Macbeth, 80, 233, 238.
MacDougall, 63.
MacIntire, 13.
MacIvor, 58, 350, 358, 365, 374, 382.
Mackay, 45.
Mackenzie, 212, 214.
Mackert, 267.
MacLaurin, 220.
Macleod, 18, 25, 34.
Mactear, 172.

- Magnus, 16, 28, 29, 136, 159, 389.
 Magnussen, 59.
 Magri, 54, 55, 267.
 Mahanti, 123.
 Mahla, 136.
 Mai, 320, 342.
 Mailfert, 300, 357.
 Mair, 353.
 Maisin, 137, 180.
 Majima, 91.
 Majler, 343.
 Makow, 192.
 Maljishoff, 30, 355.
 Mallard, 171.
 Mallet, 148, 174, 359.
 Malus, 20.
 Maly, 37, 148, 149.
 Manasse, 206.
 Manchot, 130, 155, 250, 252, 327, 328.
 Manek, 205.
 Mangun, 96.
 Manley, 168.
 Mann, 201.
 Manuelli, 38.
 Maquenne, 25, 226.
 Marc, 289, 298.
 Marcet, 262.
 Marchal, 175.
 Marchand, 21, 23, 303.
 Marchlewski, 207.
 Marculle, 12, 123.
 Marckwald, 77, 352, 362.
 Margottet, 299, 314.
 Margules, 172.
 Marie, 187.
 Marignac, 138, 145, 162-164.
 Marino, 308, 330.
 Marinot, 45.
 Marjanovid, 178.
 Marqueyrol, 45.
 Mareh, 12, 177.
 Marshall, 165, 166, 169, 181, 182, 184-186,
 212, 214.
 Marston, 13.
 Martin, 66, 105, 119, 223.
 Martini, 201.
 Marusawa, 132.
 Marx, 11, 228.
 Mason, 130, 132.
 Masson, 183, 184.
 Mathers, 332, 336, 359, 384.
 Mathews, 39.
 Mathewson, 300.
 Mathias, 88, 95, 106, 112.
 Matthews, 115, 334, 341.
 Matthey, 352, 354.
 Matthias, 35.
 Matthiessen, 354.
 Matthieu-Plessy, 199, 203.
 Mitula, 178.
 Maxted, 159.
 Maxymowicz, 365.
 May, 123, 297.
 Mayer, 120, 166.
 Mayes, 88, 100, 101.
 Mayr, 66, 99, 198, 199, 224, 283.
 Mayrhofer, 40.
 Mazzetti, 120.
 Mazzucchielli, 15, 29, 181.
 McOrea, 36, 109.
 McCrosky, 332.
 McDavid, 145.
 McGavack, 111.
 McGrath, 159.
 McHargue, 103.
 McHatton, 74.
 McIntosh, 54, 65, 169.
 McKay, 123.
 McKee, 91.
 McKenzie, 91.
 McKibbin, 13.
 McLauchlan, 52, 64.
 McLay, 299, 356.
 McLennan, 35, 36, 299, 356.
 McLeod, 84, 169, 299, 356.
 Mead, 359.
 Mecklenburg, 65, 299, 363.
 Medox, 71.
 Mehl, 353.
 Meier, 299, 330.
 Meihuizen, 39.
 Meijer, 58.
 Meilhère, 178.
 Merneke, 127.
 Meissner, 35.
 Meister, 228.
 Melikov, 187.
 Mellquist, 309, 310.
 Meloche, 385, 388.
 Melsens, 53, 105, 111, 119.
 Mencke, 115.
 Mendeléeff, 163, 165, 168, 203, 221, 360.
 Menke, 84, 367, 378, 379.
 Mente, 242.
 Merreywether, 179.
 Merrill, 322.
 Merriman, 233.
 Merz, 34, 48, 59, 352.
 Messel, 145.
 Messenger, 315.
 Messerschmidt, 299.
 Messini, 32.
 Metcalfe, 35, 299.
 Metz, 65, 223.
 Metzner, 327, 329, 333, 372, 373, 375-377,
 379, 385, 387, 390.
 ter Meulen, 45.
 Meunier, 306, 312, 329.
 Meuwisen, 236.
 Meyer, C., 14, 259.
 Meyer, F., 159, 180.
 Meyer, H., 91.
 Meyer, J., 30, 121, 126, 174, 199, 206-208,
 226-228, 230, 231, 294, 304, 307, 312,
 317, 326, 329, 331-333, 337, 341, 384.
 Meyer, L., 4, 126.
 Meyer, R., 57.
 Meyer, V., 14, 47, 55, 56, 106, 258, 259, 278.
 Michaelis, 78, 79, 81-84, 87-89, 91, 95,
 96, 98, 99, 134, 142, 221, 247, 248, 250,
 308, 316, 318, 328, 331, 374.
 Michel, 94, 336.

- Michielsen, 263.
 Michler, 50.
 Mickwitz, 301.
 Middleton, 284.
 Migliorini, 183-185.
 Miksch, 367.
 Milbaner, 15, 48, 119, 129, 170, 302.
 Miles, 110.
 Millar, 52.
 Miller, F. W., 172.
 Miller, J., 123.
 Miller, R. F., 355.
 von Miller, 50.
 Millikan, 35, 36.
 Millon, 94.
 Millott, 320, 327, 372, 373.
 Mills, 67, 69, 70, 152, 266, 269.
 Minaki, 164.
 Mindalev, 179.
 Mingoia, 131, 315.
 Minnig, 384.
 Miolati, 334.
 Miquel, 49.
 Missaghi, 27.
 Misutch, 245.
 Mitchell, 114.
 Mitscherlich, 20, 22, 29, 177, 193, 291, 296, 331.
 Mitsukuri, 259.
 Mixter, 380, 383.
 Moddermann, 159.
 Moeller, 186, 187.
 Mohr, 57.
 Moissan, 9, 18, 36-38, 52, 58, 64, 73, 74, 84-86, 225, 237, 313, 315, 326, 358, 372.
 Moldenhauer, 181, 236, 331-333, 384.
 Molengraaf, 21.
 Moles, 42, 111, 269, 286, 300, 316, 339.
 Molinari, 149.
 Molitor, 106.
 Mommers, 319, 375, 377.
 Mommsen, 194.
 Monckman, 32.
 Mondain-Monval, 18, 21, 34, 35, 37, 296.
 Mondolfo, 188.
 Monroe, 45, 260.
 Montigne, 281.
 Moody, 188.
 Mooy, de, 119.
 Moraht, 282.
 Morancé, 157.
 Morawaki, 201, 219.
 Morel, 353, 379, 380, 390.
 Morgan, 166, 168, 352, 354, 359, 360, 376.
 Mori, 84.
 Moritz, 151.
 Morrell, 45.
 Morren, 114, 250.
 Morveau, de, 135.
 Moser, 177, 308, 310, 312-314, 367, 371.
 Moss, 35, 291, 292.
 Moureu, 90.
 Mourlot, 175.
 Moutier, 29.
 Muck, 212.
 Mueller, 35.
 Mugdan, 189, 191, 192.
 Mägge, 22.
 Muir, 83, 128, 171, 172.
 Mulder, 37, 274.
 Muller, A., 323.
 Müller, E., 30, 179, 181, 182, 185, 294, 300, 306, 308, 336, 356, 359, 364, 366, 383.
 Müller, F., 174.
 Muller, F. J., 351.
 Muller, J. A., 165, 195, 209, 224.
 Müller, M., 98-100, 248, 329.
 Muller, M. E., 226.
 Müller, P. A., 52.
 Müller, W., 27, 178.
 Muller, W. J., 106.
 Muller-Erzbach, 28.
 Müllner, 193.
 Mund, 112, 113.
 Munday, 297.
 Murakami, 300.
 Muret, 96, 97.
 Murray, 169.
 Muspratt, 131.
 Mussgnug, 199.
 Muthmann, 20, 22, 23, 25, 26, 28, 235, 236, 238, 240, 291, 292, 310, 320, 330, 338, 346, 347, 350.
 Myers, 49, 55, 193, 218.
 Mylius, 45, 385, 388.
 NABL, 202, 208, 214, 225.
 Nabot, 202.
 Naef, 155, 162, 163, 165.
 Nagaoka, 356.
 Naik, 80, 94.
 Naito, 132.
 Namias, 186, 188.
 Napier, 172.
 Narugi, 178.
 Nasimi, 39, 40, 112, 138, 163, 164.
 Natta, 372.
 Naumann, 58.
 Neber, 183.
 Neller, 12.
 Némec, 303.
 Neogi, 115.
 Nernst, 14, 21.
 Nestell, 123.
 Nettlefold, 172.
 Neuberg, 201.
 Neumann, 8, 29, 32, 78, 105, 119, 149, 153, 161, 162.
 Neville, 305.
 Nichols, 36.
 Nicholson, 297, 298.
 Nickell, 162.
 Nicol, 299.
 Nicolas, 13.
 Nicolls, 9.
 Niedenführ, 152.
 Nikolai, 45.
 Nikolski, 166.
 Nilson, 288.
 Nissenson, 172.
 Njegovan, 178.

- Noack, 78, 116.
 Nobel, 137.
 Noda, 177.
 Noll, 43, 122.
 Norberg-Schulz, 131.
 Nordlander, 338.
 Nordmeyer, 21.
 Nordström, 286.
 Norris, 214, 302, 319, 340, 352, 360, 361, 367, 375, 377, 390.
 Norrish, 15, 36, 48.
 North, 88-90, 93, 94, 178, 301, 327.
 Norton, 200, 204, 228, 232.
 Nosé, 363.
 Nowakowski, 30, 294, 300, 359.
 Noyer, 27.
 Noyes, 169.
 Nukiyama, 356.
 Nydegger, 178.
 OBACH, 299.
 Oberhauser, 130.
 Oberhelman, 352, 382, 383.
 Oddo, 79, 81, 88, 91, 116, 138-140, 143, 144, 163, 164, 178.
 Odén, 30.
 Odling, 137, 203, 229.
 Odo, 39.
 O'Donogue, 266, 267.
 Oefele, 357, 390.
 von Oettingen, 194.
 Ogata, 121.
 Ogawa, 120, 243.
 Ogier, 78, 88, 92, 95, 96, 98.
 Ogilvie, 123.
 Oglialoro, 22.
 Olbrich, 184.
 Olin, 78.
 Olivari, 39, 84, 290, 305.
 Olivier, 9, 49.
 Olszewski, 54, 259, 313.
 Onnes, 63.
 Onorato, 9.
 Opl, 50.
 Oppenheim, 128, 170, 384.
 Orloff, 29, 39, 228, 232.
 Orlowaky, 60, 61, 299.
 Ormandy, 45.
 Orndorff, 39, 77.
 Ortner, 327, 328.
 Osann, 137.
 Ostersetzer, 79.
 Ostwald, 29, 30, 60, 124, 208, 215, 280, 334.
 O'Sullivan, 175.
 Otsuka, 49.
 Ott, 287.
 Ottenstein, 294, 355.
 Otto, 50, 98, 99, 207, 209, 286.
 Outcault, 122, 129.
 Overdick, 214, 224.
 PAAL, 293, 355.
 Pabst, 248.
 Paciello, 284.
 Padberg, 38, 199.
 Pagliani, 109.
 Pain, 171.
 Paine, 49.
 Palache, 174.
 Palet, 159, 306.
 Palma, 102, 231.
 Palme, 184.
 Pamfil, 119, 120.
 Pancera, 148.
 Pannain, 186, 188.
 Panzner, 162.
 Papish, 116, 364.
 Parankiewicz, 299.
 Parke, 80.
 Parker, H. G., 177, 178.
 Parker, R. G., 147.
 Parker, T. W., 325, 381.
 Parkes, A., 80.
 Parkes, A. E., 128.
 Parkes, J. W., 156.
 Parkhurst, 108, 110.
 Parmentier, 260, 262, 264.
 Parnell, 50.
 Parr, 107, 309.
 Parravano, 65, 299.
 Parsons, 69-71.
 Patel, 80.
 Partington, 12, 33, 79, 88, 100, 101, 102, 107, 137, 220, 224, 355, 379.
 Pascal, 107, 173, 221.
 Paschen, 35.
 Paternò, 15, 29, 69.
 Paton, 277.
 Patrick, 111.
 Patten, 281.
 Patterson, 127, 356.
 Pattinson, 177.
 Paul, 17.
 Pauli, 63.
 Pauling, 385.
 Pauthenier, 261.
 Pavlov, 136, 178.
 Pawletta, 331.
 Pawlewski, 92.
 Pawlow, 163.
 Payen, 22, 25.
 Peachey, 13.
 Péan de St Gilles, 28, 129, 207, 208.
 Pearson, 56.
 Péchard, 120.
 Pechmann, 205.
 Pedler, 56.
 Pedrma, 320.
 Peel, 258, 262, 344.
 Peirce, 326, 329, 377.
 Pekar, 39.
 Pélabon, 38, 48, 55, 297-300, 312, 313, 355, 363.
 Péligot, 155.
 Pellini, 290, 299, 300, 307, 320, 358, 360, 363, 366, 388, 390.
 Pelloggio, 37, 218.
 Pelouze, 127, 158, 212.
 Perciabosco, 283.
 Pérégrin, 45, 158.
 Pereira, 178.
 Perkin, 168.

- Perkins, 200, 204, 308, 367.
 Perley, 152, 162.
 Perman, 52, 124, 140.
 Pernell, 104.
 Perrot, 52, 54, 58, 297.
 Personne, 288.
 Persoz, 87, 127, 217.
 Peters, 188, 356, 367, 391.
 Petersen, 21, 23, 26-28, 37, 290, 291.
 Petertil, 44.
 Petit, 172.
 Petrelius, 185.
 Petrenko, 181.
 Petterson, 288.
 Pettersson, 303, 334, 336, 337.
 Petz, 350.
 Petzold, 45.
 Pfannmuller, 66.
 Pfaundler, 162, 164, 165.
 Pfeiffer, 22, 121.
 Pfordten, 52.
 Pfund, 298, 299.
 Pfundt, 179.
 Philip, 282.
 Philippi, 170.
 Phillips, A., 47.
 Phillips, C. E. S., 297.
 Phillips, H., 66.
 Phillips, P., 136, 159.
 Phillips, R. J., 123, 132.
 Piatti, 110.
 Piccard, 61, 204.
 Piccardi, 299, 359.
 Pickering, 165, 167, 168, 172, 201.
 Pickett, 56.
 Picon, 131, 200, 203.
 Pictet, 63, 121, 142, 163, 167, 172.
 Picton, 61, 63.
 Pierce, 58.
 Pieroni, 319.
 Pierre, 109.
 Pierron, 210, 214.
 Piersol, 298.
 Pigulewski, 19.
 Pihlblad, 36.
 Pilipenko, 286.
 Pincussen, 13.
 Pinkard, 116.
 Pintza, 106.
 Piotrowski, 91, 120, 142, 243, 253.
 Piria, 56.
 Pisati, 15, 19, 21, 34.
 Pissarjewski, 187.
 Pitkin, 172.
 Pitman, 172.
 Platzmann, 18, 19.
 Plauchud, 49.
 Playfair, 350.
 Plessy, 210, 217.
 Plotnikov, 59.
 Plucker, 35, 299.
 Plüddemann, 136, 137, 161, 175.
 Plyron, 60.
 Pochettino, 293, 295, 298.
 Poggendorff, 370.
 Pohl, 60, 136, 139, 297, 298.
 Pohland, 270.
 Pohorecka-Lelesz, 45.
 Pokrowski, 32.
 Pólányi, 110.
 Polgrean, 301.
 Pohakov, 137.
 Pollacci, 37, 148.
 Pollak, 80.
 Pollitt, 161.
 Polt, 162.
 Pomeroy, 208, 210.
 Pomilio, 170.
 Pool, 318.
 Pope, 40, 82, 91, 305, 316.
 Popoff, 24, 39.
 Popp, 201.
 Porret, 278.
 Porritt, 66.
 Porter, 35, 141, 145, 150.
 Portevin, 118, 148.
 Portillo, 213.
 Potiltzen, 300.
 Potter, 384.
 Pound, 169.
 Pounder, 131.
 Powell, 254.
 Pozzi-Escott, 49, 205.
 Prætorius, 255, 391.
 Prandtl, 95-97, 301, 320, 324, 358, 375.
 Pranschke, 116.
 Pratesi, 62.
 Preibisch, 253.
 Preher, 137.
 Preuner, 15, 52, 55, 289.
 Prevot, 61, 63.
 Previe, 112.
 Prevostaye, 250.
 Price, T. S., 35, 40, 184-186, 189-192, 203, 339.
 Price, W. J., 248, 250, 251.
 Prichard, 93.
 Prideaux, 74, 315, 316, 318, 320, 327, 372, 373.
 Priestley, 103.
 Prinz, 99, 113, 308, 310, 367.
 Pritze, 330.
 Proskouriakoff, 171.
 Prost, 149.
 Prothière, 49.
 Prud'homme, 95, 228.
 Pruner, 84.
 Prytz, 52, 60.
 Puchner, 29.
 Pullinger, 171.
 Pulsifer, 45.
 Purgold, de, 100.
 Putnam, 364.
 QUAM, 53, 55, 58.
 Quantin, 178.
 Quincke, 19.
 RAAB, 255.
 Rabe, 152.
 Raffo, 30, 32.
 Railton, 98.

- Rajagopalan, 133, 193, 195.
 Rakowicz-Pogorzelska, 356.
 Raleigh, 63.
 Rakston, 54, 55, 58.
 Rammeisberg, 200, 207, 210, 292.
 Ramsay, 14, 34, 35, 40, 68, 163, 176, 190,
 315, 316, 318, 320.
 Rancken, 35.
 Randall, 16, 33, 116, 166.
 Ranfaldi, 20.
 Rankin, 18.
 Rankine, 123, 298.
 Rao, 282.
 Raschig, 127, 135, 154, 178, 192, 214, 215,
 217-220, 222, 230, 242-247, 249, 251-
 253.
 Rassow, 258.
 von Rath, 84, 338.
 Rathke, 23, 207, 210, 273, 291-293, 296,
 338, 339, 342, 344.
 Rawling, 185.
 Ray, B. B., 36.
 Ráy, P., 133.
 Ray, W. L., 321, 322.
 Raynaud, 291.
 Rebs, 68, 139.
 Reckendorfer, 13.
 Recours, 173.
 Réceci, 45.
 Reese, 126, 159.
 Regnault, 63, 94, 107, 112, 241, 259, 260,
 292, 353, 354.
 Reicher, 23.
 Reichenstein, 306, 359.
 Reid, 309, 315.
 Reimlinger, 155, 252.
 Reinders, 132.
 Reinhardt, 161.
 Reinhold, 64.
 Remking, 208.
 Reinoso, 166.
 Reinsch, 49.
 Reismann, 56.
 Resenschack, 355-357, 366, 367, 384.
 Retgers, 173, 291.
 Reubke, 242.
 Reychler, 110.
 Reyl-Pailhade, de, 49.
 Reynolds, 154, 201, 274, 281, 329.
 Rhead, 254, 256.
 Rhein, 295.
 Ribaut, 49.
 Ricca, 186.
 Ricevuto, 10.
 Richards, 42, 43, 177, 178.
 Richardson, 169.
 Richarz, 180, 181.
 Richmond, 163, 165, 179.
 Richter, 63.
 Rideal, 15, 36, 48.
 Riding, 59, 67.
 Riecke, 14.
 Riegel, 95-98.
 Ries, 122, 160, 298, 301.
 Riesenfeld, 63, 102, 175, 204, 213, 215, 218,
 223, 224.
 Rimini, 187.
 Ringborn, 133.
 Ringer, 338.
 Rink, 278.
 Riou, 110.
 Ripper, 177.
 Ritsema, 262.
 Rittener, 60.
 Ritter, 370.
 Rive, de la, 109.
 Rivett, 131.
 Rivlin, 32.
 Rjabinin, 103.
 Robbs, 171, 172.
 Roberts, 43, 92, 94, 299, 364.
 Robertson, 13, 112.
 Robinson, H., 36.
 Robinson, P. L., 67, 69, 70, 163, 166, 258,
 262, 266, 269, 325, 344, 381.
 Robson, 160.
 Rochleder, 207.
 Rogers, 44, 172.
 Rohland, 29.
 Rohn, 307, 329.
 Röhrig, 131, 135.
 Rolla, 313, 314.
 Rolland, 350.
 Romani, 181.
 Rondier, 249.
 Ronnet, 283.
 Roozeboom, 24, 77, 82, 84, 109.
 Roscoe, 162.
 Rose, Heinrich, 58, 81, 83, 95, 141, 142, 177,
 193, 244, 248, 250, 288, 301, 324, 329,
 336, 353, 373, 380, 381.
 Rose, Hermann, 22.
 Rosen, 36, 297, 299, 356.
 Rosenfeld, 67, 300.
 Rosenheim, 134, 199, 279, 303, 328, 330,
 360, 366, 368, 385, 387, 388.
 Rosenkränzer, 65.
 Rosenstiehl, 95, 97, 286.
 Rosental, 32.
 Rosenthaler, 129.
 Rosse, 298.
 Rossi, 32.
 Rossignol, 152.
 Rossing, 64.
 Roth, 178, 232, 352, 353.
 Rothe, 16.
 Rotinjan, 19.
 Rousseau, 165.
 Royer, 25.
 Rubens, 107.
 Rubies, de, 286, 316.
 Rück, 279.
 Rücker, 165.
 Rudge, 19, 34.
 Rudolphi, 280.
 Rudorff, 174.
 Ruedy, 35.
 Ruer, 172.
 Ruff, 29, 35, 38, 39, 76, 80-86, 92-94, 99,
 128, 194, 211, 234-237.
 Rühle, 139, 140.
 Ruhmer, 301.

NAME INDEX.

Rule, 59, 62, 67, 72.

Rumpf, 64.

Runge, 35.

Russell, E. J., 119, 120, 136, 261, 271.

Rytel, 196, 199.

SABALITSCHKA, 131, 132.

Sabanéeff, 253, 254.

Sabatier, 25, 27, 59, 67, 68, 248, 251, 252, 348, 349.

Sabbatini, 28.

Sacco, 303, 317, 326.

Sacerdote, 54.

Sacher, 60.

Sack, 363.

Saint-Pierre, 211.

Saito, 363.

Salathe, 103, 104, 136, 249.

Salauze, 182.

Saldau, 363.

Sale, 298.

Salet, 15, 35, 36, 299, 356.

Salkin, 102.

Salkowski, 49.

Salla, 91.

Saloman, 25, 270.

Salzer, 217.

Sand, 284.

Sander, 127, 130, 206, 213, 216, 223.

Sanders, 117.

Sandmeyer, 258.

Sandonnini, 132.

Sandorfy, 286.

Sanfourche, 249.

Sanger, 95-98.

Saposchnikoff, 165.

Sartorius, 117.

Sasaki, 49.

Saunders, 291, 292.

Sawyer, 299.

Sayce, 296.

Scagliarini, 62, 186, 188.

Scala, 39.

Scandola, 163, 164.

Schafarik, 380.

Schäfer, 310, 320, 330.

Schall, 14, 182.

Schander, 49.

Schär, 225, 227.

Schaum, 15, 16, 18.

Scheel, 166.

Scheele, 135.

Scheerer, 21, 23.

Scheffer, 58.

Scheidler, 253.

Schelle, 352.

Schellhaas, 181.

Schenck, 71, 115, 138, 140, 233, 235.

Scheneffeld, 131.

Scheringa, 64, 158.

Schertel, 153, 162, 163.

Scheuer, 41.

Scheurer-Kestner, 104, 116, 136, 146, 172, 286.

Schiff, 29, 60, 87, 91, 99, 114, 120.

Schifferdecker, 81-83, 95.

Schikorr, 32.

Schilov, 79.

Schinn, 309.

Schlagdenhauffen, 262.

Schlesinger, 249.

Schliebs, 152.

Schluck, 367.

Schlundt, 88, 92.

Schmerda, 281.

Schmid, 115, 172, 228, 250, 353, 376.

Schmidt, E., 59, 68, 119, 143.

Schmidt, E. A., 306.

Schmidt, M., 309.

Schmidt, O., 199.

Schmedel, 152.

Schmitz-Dumont, 28, 263.

Schneider, 18, 34, 35, 65, 168, 277, 278, 318, 319, 350.

Schoch, 178.

Schoenmaker, 138, 140.

Schollenberger, 13, 45.

Schollhorn, 49.

Scholz, 19, 31.

Schon, 45, 66.

Schönben, 21, 128.

Schönfeld, 52, 108, 124.

Schönherr, 170, 181.

Schorlemmer, 203.

Schott, 329.

Schramm, 121.

Schrauf, 21.

Schrenk, 308, 367.

Schroder, 111, 116, 121, 143, 346, 347, 350.

Schroedter, 148.

von Schrott, 291, 298.

Schrotter, 351.

Schubert, 137.

Schuetze, 77.

Schuhmann, 6, 353, 359, 380.

Schulek, 199, 205.

Schuler, 131.

Schuller, 352.

Schulte, 257.

Schultz, 173.

Schultz-Sellack, 137, 138, 140, 142-144, 147, 148.

Schultze, 120.

Schulz, 256.

Schulze, A., 259.

Schulze, H., 109, 119, 143, 147, 293, 327, 329, 339, 340.

Schulze, P., 121.

Schumann, H., 243.

Schumann, O., 60, 63, 247, 248, 250.

Schupp, 15, 52, 55.

Schürmann, 61.

Schuster, 57.

Schütz, 38.

Schützenberger, 87, 95, 104, 225, 226, 228, 229.

Schwarz, 37, 61, 178, 229.

Schweitzer, 128.

Schwicker, 135, 188, 203, 283.

Seichilone, 34.

Sconzo, 143, 144.

Scott, 14, 44, 165, 174.

- Seal, 279.
 Schrell, 13.
 Sedlacek, 302.
 Seelig, 270.
 Seguin, 35.
 Seidel, 124, 196, 232.
 Seitter, 238, 240.
 Seka, 170.
 Selchow, 43, 364.
 Selezner, 31, 38.
 Seliber, 175.
 Selmi, 27, 158.
 Selmons, 127.
 Semenov, 103.
 Senderens, 37-39, 193, 300, 359.
 Serra, 39, 79.
 Sestini, 84, 113, 248.
 Seubert, 206.
 Seyer, 109, 113.
 Seyewetz, 132, 227, 232, 263.
 Shah, 94.
 Sharer, 36.
 Shaw, 13, 219, 309, 315.
 Shearer, 108, 124.
 Sherrill, 329.
 Sherry, 113.
 Sherwood, 108.
 Shilov, 61.
 Shilton, 57.
 Shimidzu, 8, 50, 126, 134, 193, 350.
 Shimosé, 224, 288, 289, 316, 338, 350, 351, 357, 370, 379, 389.
 Shinn, 199.
 Shipsey, 13.
 Shukla, 40.
 Sidot, 261.
 Siecke, 270.
 Siedler, 256, 257, 352, 353.
 Sieg, 355.
 Siegbahn, 299, 356, 361.
 Siegert, 330.
 Siegmund, 228.
 Siemens, 297, 298.
 Sieverts, 115.
 Silbermann, 27.
 Silberrad, 80, 94.
 Silverman, 301.
 Silvestri, 21, 22.
 Simanuki, 91.
 Simek, 354.
 Simon, 13, 45, 80, 96.
 Simons, 318.
 Simpson, 50, 104.
 Sims, 100, 108, 124.
 Sinnatt, 228.
 Sirks, 299.
 Sisco, 363.
 Skey, 63.
 Skoglund, 152.
 Skowronski, 166.
 Skrabal, 127, 199.
 Skraup, 32.
 Slater, 201.
 Smedt, de, 259.
 Smiles, 40, 203.
 Smith, A., 15-21, 27, 28, 84.
 Smith, A. L., 277.
 Smith, C. J., 107, 123, 271.
 Smith, C. R., 279.
 Smith, D. F., 93, 166.
 Smith, E. A., 44.
 Smith, E. F., 79.
 Smith, G. B. L., 275, 276, 321, 322, 356.
 Smith, G. F. H., 233.
 Smith, G. McP., 60, 63.
 Smith, H. G., 36, 299, 356, 366.
 Smith, J. F., 286.
 Smith, J. H., 129, 232.
 Smith, N., 119, 120, 136.
 Smith, N. D., 281.
 Smith, R. A., 148.
 Smith, W., 116, 172, 215-217, 219, 297, 310.
 Smith, W. T., 108, 110.
 Smite, 16, 119, 138, 140, 281.
 Smoluchowski, 296.
 Smythe, 72, 116, 117, 128.
 Snelling, 389.
 Snow, 36.
 Snyder, 45.
 Sobrero, 27.
 Söderbäck, 276.
 Sokolow, 207.
 Somiya, 147, 179, 251.
 Sommer, 192, 243, 254.
 Sondag, 227, 232.
 Soni, 58.
 Sonstadt, 201, 214.
 Sorel, 153, 166.
 Sorrentino, 113.
 Sosman, 35.
 Soubairan, 233.
 Souder, 151.
 Spacu, 283.
 Spangler, 151, 162.
 Späth, 298.
 Spelta, 307.
 Spence, 226.
 Speransky, 253.
 Spica, 25.
 Spielmann, 263.
 Spilker, 9.
 Spring, 22, 28, 61, 67, 121, 134, 194, 196, 197, 201, 207, 209-212, 214-217, 219, 354.
 Squantani, 330.
 Stafford, 15.
 Stahl, 287.
 Stähler, 361.
 Stanek, 64.
 Stark, 35, 39, 181.
 Stas, 42.
 Staudenmaier, 380, 383-385, 389.
 Stavenhagen, 142.
 Stavorinus, 45, 66.
 Steele, 50, 54, 55, 113.
 Steenberg, 158.
 Stehlík, 354.
 Stehmann, 185.
 Stein, 224.
 Steiner, 304, 327, 334, 352, 359.
 Steinhäuser, 199.
 Steinkopf, 84.

- Steinmetz, 45, 279.
 Stephens, 256.
 Steubing, 15, 299, 356.
 Stevens, E. H., 260.
 Stevens, H. P., 13, 284.
 Stevens, W. H., 13.
 Stewart, 63, 117, 169, 313.
 Stiles, 107.
 Stingl, 201, 219.
 Stock, 29, 112, 255, 270, 344, 391.
 Stöcker, 163, 333.
 Stokes, 134.
 Stolba, 103, 383.
 Stoll, 19.
 Stolte, 346.
 Stommel, 179.
 Stone, 159.
 Stortenbeker, 173.
 Stover, 302, 360.
 Stowe, 113.
 Stratton, 33.
 Strecker, 72, 81, 91, 134, 317, 319, 323, 340, 341, 375, 377.
 Streit, 45.
 Strenk, 73.
 Stromeyer, 286.
 Strong, 19.
 Struve, 42.
 Strzoda, 157.
 Stubbs, 115.
 Stuer, 242.
 Svanberg, 42.
 Svedberg, 32.
 Sweeney, 122, 129.
 Swezey, 275, 276.
 Swift, 329.
 Swoboda, 45.
 Sydow, 213, 223, 224.
 Sylvester, 118.
 Syrkin, 175.
 Szarvasy, 289.
 Szentpaly-Peyfuss, 224.
 von Szilágyi, 199.
 TABOURY, 120, 286.
 Taft, 113.
 Takamatsu, 215-217, 219.
 Talenti, 178.
 Tamayo, 30.
 Tammann, 23, 24, 33, 109, 123, 259.
 Tartar, 37.
 Tarugi, 60, 183-189, 202, 210, 267, 282.
 Tatlock, 172.
 Taurel, 27.
 Taylor, E. R., 257.
 Taylor, F. D., 169.
 Taylor, H. A., 56, 116.
 Taylor, I., 48.
 Taylor, J., 279.
 Taylor, W. H., 154.
 Taylor, W. W., 318.
 Teitelbaum, 310.
 Templin, 192, 243.
 Terlinok, 77, 92.
 Terrasse, 39, 77.
 Terres, 214, 224.
 Tesch, 361.
 Testoni, 178.
 Thalen, 356.
 Than, 269.
 Thatcher, 37, 201, 214-216.
 Thénard, 68.
 Thesmar, 228.
 Thiel, 85, 127, 177.
 Thilo, 163, 167.
 Thirring, 297, 301.
 Thomann, 47.
 Thomas, E., 61, 204.
 Thomas, F., 19.
 Thomas, J. S., 59, 67, 72, 166.
 Thomas, M. D., 123.
 Thomaschek, 63.
 Thomason, 359.
 Thomsen, 6, 37, 52, 56, 59-61, 78, 92, 93, 107, 112, 124, 126, 136, 139, 141, 165, 168, 194, 208, 212, 215, 218, 260, 279, 317, 318, 327, 331, 358.
 Thomson, 32, 88, 93, 126, 220, 286.
 Thorn, 158.
 Thorpe, 40, 81, 86, 91, 99, 250, 259.
 Threlfall, 12, 23, 27, 32, 289.
 Thwing, 32.
 Tibbals, 354, 358, 363.
 Tiede, 63.
 Tilden, 248.
 Timár, 9.
 Timofejoff, 39.
 Tipler, 220.
 Tissot, 60.
 Tite, 165.
 Tocco, 62.
 Toepler, 23, 34.
 Tolloczko, 39.
 Tolman, 169.
 Tomiček, 308, 364, 368.
 Tomkinson, 115.
 Tomoshuge, 300.
 Topalov, 224.
 Toquet, 45.
 Torelli, 186, 188.
 Town, 321, 322.
 Townshend, 259.
 Traube, 33, 40, 86, 115, 143, 169, 170, 187, 188, 241, 242, 245.
 Trautmann, 49.
 Trautz, 76-78, 101, 155, 252.
 Treadwell, 44, 66, 283.
 Treves, 36.
 Trevor, 169.
 Trey, 208.
 Tribe, 169.
 Troost, 14, 27, 34, 289, 296, 354.
 Troschel, 148.
 Tschelinzov, 169.
 Tschermak, 21.
 Tschugaev, 300, 358.
 Tubandt, 64.
 Tucek, 119.
 Tucker, 12, 35.
 Tungay, 146, 151.
 Turner, 42, 177, 359.
 Turrentine, 185.

Tuttle, 44.
 Tutton, 173, 335-337.
 Twiss, 13, 19, 35, 40, 203, 339.
 Tykač, 45.
 Tykocynier, 123.
 URBALINI, 27.
 Uchida, 132.
 Udden, 299.
 Uhler, 356.
 Umino, 354.
 von Unruh, 259.
 Urba, 380, 390.
 Urban, 385.
 Urech, 273.
 Urfer, 136.
 Uschinsky, 60.
 Usher, 42, 233, 234, 236.
 Utzino, 31.
 VALBAN, 267.
 Valdés, 232.
 Valenta, 35, 299.
 Valentine, 135.
 Valetton, 219.
 Vallance, 189.
 Valson, 174.
 Vanino, 63, 199.
 Vansteenberger, 178.
 Vanzetti, 39.
 Vaubel, 112, 163, 178, 200, 289.
 Vauquelin, 57.
 Veley, 168.
 Venkataramaiah, 282.
 Verneuill, 318, 345-347.
 Vernon, 147, 163, 369, 372.
 Verola, 161.
 Vesper, 66.
 Vieille, 318.
 Vila, 170.
 Vilbrandt, 131.
 Villard, 109.
 Villiers, 169, 198, 210, 214.
 Villiger, 93, 170, 183, 184, 189-191.
 Vincent, 350.
 Vio, 358, 390.
 Violette, 286.
 Vitelli, 183, 187, 202, 210.
 Vlastimil, 178.
 Vles, 132.
 Vogel, F. C., 141, 142.
 Vogel, H., 29.
 Vogel, I., 12, 101, 102, 137, 222, 224.
 Vogel, R., 198.
 Vogelenzang, 178.
 Voghera, 194.
 Vohl, 43, 201, 202.
 Volhard, 115, 274, 282, 283.
 Vorländer, 127.
 Vorobiev, 45.
 Vortmann, 38, 60, 199, 200, 214, 217.
 Vornessenski, 233-236, 238.
 Vrevski, 166.
 Vuilleumier, 73.
 Vulquin, 179.
 Vykypiel, 45, 66.

WAALS, van der, 108.
 Wackenroder, 128, 217, 220.
 Wagenknecht, 263, 265, 380, 384, 386.
 Wagenmann, 149.
 Wagner, 45, 134, 158, 192, 333, 334, 341.
 Wakefield, 367.
 Wakaman, 13.
 Walbaum, 121.
 Walden, 88, 92, 93, 113, 114, 164, 203.
 Walerstein, 36, 299, 356.
 Walker, 106, 107, 201.
 Walsh, 130, 132.
 Walton, 68-71.
 Wandenbulcke, 201.
 Wanjukow, 175.
 Wanklyn, 163, 166.
 Warburton, 354.
 Wardlaw, 116-118, 128.
 Warner, 105, 170.
 Warren, 123, 174, 335.
 von Wartenberg, 14, 15, 107, 114, 289, 355.
 Wassermann, 353.
 Waterman, 130.
 Watson, 37, 45, 133, 193, 195.
 Watts, 179.
 Wavre, 224.
 Webb, 248, 250, 251.
 Weber, 16, 28, 76, 127, 138, 139, 142, 164,
 224, 247, 248, 250, 251, 312, 318, 327,
 338, 370, 376, 379, 389.
 Webster, 273.
 Weeldenburg, 267, 271, 272.
 Weil, 66, 302.
 von Weimarn, 19, 29-31, 355.
 Weinheber, 366, 368, 387, 388.
 Weinland, 64, 373.
 Weintraub, 248.
 Weise, 254, 295.
 Weiser, 62, 119, 364.
 Weissenberger, 99, 110.
 Weith, 59.
 Weitz, 220.
 Weizel, 107.
 Welde, 201.
 Weldon, 174.
 Welke, 110.
 Weller, 326.
 Wells, 283, 306, 350, 373.
 Welter, 206, 208.
 Wendehorst, 313, 335.
 Wenger, 136.
 Wentzki, 154, 155, 252.
 Werner, 281.
 Wernich, 121.
 Wertheim, 179, 267.
 Wesley, 116.
 West, 189, 191.
 Westmoreland, 202.
 Wetherell, 25.
 Wheeler, 254, 256, 375, 377, 378.
 Whetham, 169.
 Whitaker, 26.
 White, 12, 261.
 Whitehead, 352, 371.
 Whitford, 68, 70.
 Whitmore, 363.

- Wibaut, 254, 256.
 Wiebe, 21, 22.
 Wiedemann, 52, 108.
 Wieland, 136, 161.
 Wieler, 121.
 Wien, 259.
 Wigand, 16, 18-21, 32, 33.
 Wijk, van der, 250.
 Wilcoxon, 275.
 Wilczewski, 119, 149.
 Wilde, 136.
 Wildish, 322.
 Wilhelm, 131.
 Wilke-Dörfurt, 67.
 Wilkes, 232.
 Wilkinson, 11, 12, 54, 55, 59.
 Will, 49.
 Willard, 66, 308.
 Willfroth, 344.
 Williams, R. C., 12, 13.
 Williams, S., 98.
 Williams, W. C., 35, 296, 354, 377.
 Williamson, A. W. W., 203.
 Williamson, F. S., 174.
 Williamson, R., 91, 98.
 Willis, 373.
 Wills, 361, 380.
 Willstätter, 186, 191, 192, 202, 210, 212.
 Wilmet, 65.
 Wilson, A., 36.
 Wilson, J. R., 60.
 Wilson, R. W., 145, 168.
 Wilson, W. E., 109.
 Windaus, 204.
 Winkelmann, 259.
 Winkler, 31, 50, 53, 66, 121, 136, 153, 177, 199, 248.
 Winterfeld, 83, 84, 236.
 Winterl, 278.
 Wise, 324.
 Withion, 131.
 Withrow, 122, 129.
 Wittek, 300.
 Wittwer, 278.
 Wöber, 68.
 Wohler, 29, 58, 78, 119, 128, 136, 137, 161, 175, 287, 359, 371, 375.
 Wohlgemuth, 9.
 Wölbling, 235, 238, 240.
 Wolesenaky, 45, 323, 340, 382, 383.
 Wolff, 183.
 Wolfenstein, 183, 191, 192.
 Wollak, 179.
 Wolters, 137.
 Wolvekamp, 284.
 Wood, 299.
 Woodhouse, 80, 91.
 Woodstock, 388.
 Woodward, 45.
 Worley, 177.
 Woronin, 245.
 Worsley, 325, 331, 337.
 Wourtsel, 41, 55.
 Wrede, 309.
 Wright, 63, 83, 84, 107, 124, 125, 320.
 Wroblewski, 259.
 Wällner, 259, 374, 375.
 Wunderlich, 86.
 Wurtz, 87, 88.
 Wuyts, 313.
 Wyckoff, 174.
 Wyruboff, 173.
 YAMASAKI, 179.
 Yeoman, 267, 269.
 Young, C. A., 8.
 Young, H. C., 12, 13.
 Young, J., 121.
 Young, J. F. T., 299.
 Young, L. H., 259.
 Yost, 130, 185, 208, 210, 329.
 ZAHN, 107.
 Zahorka, 127.
 Zakowski, 38, 59.
 Zambonini, 174.
 Zaprometov, 179.
 Zatzek, 201, 208, 211.
 Zawadski, 61.
 Zay, 66.
 Zeise, 262, 274.
 Zenghelis, 57, 60.
 Zickendraht, 19, 34.
 Zimmermann, 202.
 Zinke, 101.
 Zink, 179.
 Zoder, 99.
 von Zombory, 185, 188.
 Zoppellari, 299.
 Zorn, 91.
 Zschiegner, 45.
 Zschiesche, 207.
 Zumstein, 356.
 Zundel, 228.
 Zvegintzov, 17, 76.

SUBJECT INDEX.

- ALLOTELLURIC acid**, 385.
Altaite, 350.
Aluminium selenide, 314.
Alums, 174, 337.
Amidopermonosulphuric acid, 192.
Amidosulphinic acid, 120, 243.
Amidosulphonic acid, 243, 244.
Ammonium amidosulphinate, 120, 243.
 — **amidosulphonate**, 244, 253.
 — **amyselenite**, 328.
 — **chlorosulphonate**, 99.
 — **chlorotellurite**, 374.
 — **dithiocarbamate**, 274.
 — **dithioformate**, 265.
 — **ethylselenite**, 327.
 — **imidosulphonate**, 244.
 — **molybdotellurates**, 388.
 — **nitrilosulphonate**, 244.
 — **oxytriselenophosphate**, 343.
 — **perthiocarbonate**, 269.
 — **selenibromide**, 320, 341.
 — **selenite**, 330.
 — **selenocyanate**, 346.
 — **selenosamate**, 327.
 — **thiocarbonate**, 266.
Anhydrotellurates, 387.
Antimony selenides, 300.
Arsenotellurite, 351.
Aurum paradoxum, 351.
Azido carbon disulphide, 275.
Azidodithiocarbonic acid, 275.
- BARIUM** dioxyselenophosphate, 343.
 — **selenate**, 336.
 — **selenic acid**, 336.
 — **selenocyanate**, 346.
 — **tellurite**, 383.
Bismuth selenides, 300.
Black sulphur, 8, 29.
 "Blue acid," 252.
Blue sulphur, 29.
- CADMIUM** selenide, 314.
 — **tellurite**, 383.
Cæsium triselenocyanate, 346.
Calaverite, 350.
Calcium oxyselenophosphate, 343.
 — **selenate**, 336.
 — **selenocyanate**, 346.
Calgoorlite, 350.
Carbamide tellurate, 388.
Carbon bromoselenides, 344.
 — **bromosulphide**, 273.
 — **dischlorosulphide**, 272.
 — **diselenide**, 343.
 — **disulphide**, 255–275.
- Carbon disulphide**, Action of chlorine on, 272.
 — — —, **Chemical properties**, 261.
 — — —, **Detection**, 263.
 — — —, **Dissociation**, 261.
 — — —, **Estimation**, 263, 264.
 — — —, **Manufacture**, 256, 257.
 — — —, **Physical properties**, 258–261.
 — — —, **Physiological properties**, 264.
 — — —, **Preparation**, 256.
 — — —, **Reduction products**, 264, 265.
 — — —, **Thiohydrates of**, 266.
 — — —, **Uses**, 264.
 — **hexachlorosulphide**, 273.
 — **monosulphide**, 255.
 — **oxyselenide**, 344.
 — **oxysulphide**, 269–272.
 — — —, **Formation**, 269.
 — — —, **Properties**, 270–272.
 — **subselenides**, 344.
 — **subsulphide**, 255.
 — **sulphides**, 254, 255.
 — **sulphidoselenide**, 344.
 — **sulphidotelluride**, 391.
 — **tetrachlorosulphide**, 272, 273.
Carbonyl sulphide, 269.
Chloroselenic acid, 325.
Chlorosulphonic acid, 97.
Chlorothiocarbonyl sulphur chloride, 272, 273.
Chromotellurates, 388.
Clausthalite, 286.
Cobalt tellurite, 383.
Coloradoite, 350.
Coolgardite, 350.
Copper ammonium tellurite, 383.
 — **selenate**, 336.
 — — — **ammoniates**, 336.
 — **selenocyanate**, 346.
Crookesite, 286.
Cupric thiocyanate, 282.
Cuprous selenide, 300.
 — **thiocyanate**, 282.
Cyanogen compounds with hydrogen sulphide, 285.
 — **diselenide**, 345.
 — **monoselenide**, 345.
 — **monosulphide**, 277.
pseudo-Cyanogen sulphide, 281.
Cyanogen triselenide, 346.
 — **trisulphide**, 278.
- DIAMMONIUM** imidosulphonate, 244.
Diantipyril selenide, 346.
Dihydrazine sulphate, 253.
Dihydrosulphazotinic acid, 247.

- Dihydroxylamidodisulphonic acid, 247.
 Dihydroxylamine sulphonic acid, 243.
 Dimethyltelluronium dihalides, 369.
 Diphenyl telluride, 374.
 Diphenylselenone dicarboxylic acid, 333.
 Diselenotriethionine acid, 340.
 Disulphur dibromide, 83.
 — dichloride, 76.
 — difluoride, 73.
 — dithiocyanate, 278.
 Ditellurous acid, 382.
 Dithiocarbamic acid, 274.
 Dithiocyanic acid, 284.
 Dithioformic acid, 265.
 Dithiolcarbonic acid, 266.
 Dithionates, 206-210.
 Dithionic acid, 206-209.
 Dithiotetrathiazyl chloride, 238.
 Dividensite, 350.

 EMMONSITE, 350.
 Ethyl mercaptan, 268.
 — selenite, 331.
 Ethylthiolthioncarbonic acid, 268.
 Eucairite, 286.

 FERRIC thiocyanate, 282.
 Ferrotellurite, 350.
 Ferrous selenate, 337.
 Fluorosulphonates, 86.
 Fluorosulphonic acid, 86.

 GRAPHIC tellurium, 350.
 Group VIB elements, 1-7.
 — — —, Halogen compounds, 5.
 — — —, Hydrides, 4.
 — — —, Oxides, 6, 7.
 Guamdine molybdotellurate, 388.
 — thiocyanate, 274.
 — tungstotellurate, 388.

 HESSITE, 350.
 Hexamethylenetetramine tellurate, 388.
 Hexasulphamide, 237.
 Hexathionates, 220.
 Hexathionic acid, 220.
 Hydrazine alum, 254.
 — amidosulphonate, 254.
 — chromium alum, 254.
 — disulphinic acid, 253.
 — dithionates, 254.
 — hydrosulphide, 253.
 — pyrosulphite, 253.
 — sulphates, 253.
 — sulphite, 253.
 Hydrogen disulphide, 71.
 — hexasulphide, 47, 68.
 — pentasulphide, 70.
 — "persulphide," 69.
 — selenibromide, 319.
 — selenide, 312, 313.
 — — —, Heat of formation, 5.
 — sulphide, 47-67.
 — — —, Chemical properties, 55.
 — — —, Detection, 65.
 — — —, Estimation, 65, 66.

 Hydrogen sulphide, Formation, 48-51.
 — — — generator, 51.
 — — —, Heat of formation, 5.
 — — —, History, 48.
 — — —, Liquid, 54.
 — — —, Oxidation, 56, 58.
 — — —, Physical properties, 52.
 — — —, Physiological action, 60.
 — — —, Purification, 51.
 — telluride, 370-372.
 — — —, Heat of formation, 5.
 — trisulphide, 70.
 Hydrosulphites, 102, 227.
 —, Applications, 229.
 —, Constitution, 229.
 —, Estimation, 232.
 Hydrosulphuric acid, 47, 59.
 Hydrosulphurous acid, 124, 128, 225, 226.
 — — —, Constitution, 229-231.
 Hydroxylamine amidosulphonate, 253.
 — disulphonic acid, 243, 246.
 — isodisulphonic acid, 246.
 — dithionate, 253.
 — monosulphonic acid, 245.
 — sulphates, 252, 253.
 — -sulphonic acids, 243, 245, 246.
 — isosulphonic acids, 192, 243, 246.
 — trisulphonic acid, 246.
 Hyposulphurous acid, 225.

 IMIDODISULPHAMIDE, 241, 242.
 Imidosulphinamide, 241.
 Imidosulphonic acid, 243-245.
 Iron pyrites, 9, 11, 149, 150, 287.
 Iron selenides, 314.

 JOSÉITE, 350.

 LEAD dithiodi-imide, 234, 237.
 — selenocyanate, 347.
 — tellurite, 383.
 Leaf tellurium, 350.
 Lehrbachite, 286.

 MAGNESIUM dioxidiselenophosphate, 343.
 — selenate, 336.
 — selenide, 314.
 — selenocyanate, 347.
 — tellurite, 383.
 Magnolite, 350.
 Manganous tellurite, 383.
 Mellone, 285.
 Melonite, 350.
 Mercuric selenite, 330.
 — selenocyanate, 347.
 — thiocyanate, 282.
 Mercurous selenocyanate, 347.
 Mercury dithiodi-imide, 234, 237.
 Metabisulphites, 131.
 Methane, 265.
 Methyl mercaptan, 265.
 — methylxanthate, 268.
 — sulphide, 268.
 — tetrathio-oxalates, 268.
 — trithiocarbonate, 268.
 Molybdoselenites, 330.

Molybdotellurates, 388.
Montanite, 350.

NAGYAGITE, 350.

Nickel selenide, 314.

— tellurite, 383.

Nitrosulphonic acid, 243, 245.

Nitrogen bromosulphide, 239.

— chlorosulphide, 238.

— pentasulphide, 236.

— persulphide, 236.

— sulphide, 233-236, 239.

— —, Action on "sulphur dichloride," 239.

— —, Additive products, 235.

— —, Constitution, 235, 236.

— —, Preparation, 233.

— —, Properties, 233-235.

Nitrosulphonic acid, 252.

Nitrosodisulphonic acid, 251.

Nitrosohydroxylamine-sulphonic acid, 246.

Nitrososulphonic acid, 246.

Nitrososulphuric acid, 247.

Nitrosulphamide, 241.

Nitrosulphonic acid, 247-249.

— —, Constitution, 249.

— —, Properties, 248.

— anhydride, 250.

Nitrosulphonyl chloride, 250.

Nitrosulphuric acid, 251.

Nitrosylselenic acid, 341.

Nitrosylsulphuric acid, 154, 247.

Nitrosylsulphuryl chloride, 250.

Nitroxysulphuric acid, 155.

OLEUM, 144, 287, 288.

Onofrite, 286.

Orthotelluric acid, 384, 387.

Oxy-selenophosphates, 342, 343.

PARA-SULPHAT-AMMON, 244.

Pentathionates, 218.

Pentathionic acid, 217-220.

— —, Constitution, 221.

— —, Estimation, 223.

— —, Preparation, 217.

— —, Properties, 218.

Perdisulphates, 181-188.

— —, Detection, 187.

— —, Estimation, 187, 188.

— —, Properties, 183-186.

Perdisulphuric acid, 181-188.

— —, Constitution, 186.

Permonosulphuric acid, 188-192.

— —, Constitution, 191.

— —, Detection, 192.

— —, Estimation, 192.

— —, Preparation, 188, 189.

— —, Properties, 190.

Peroxylaminic acid, 251, 252.

Perselenic acid, 337.

Persulphuric acids, 181-192.

Persulphuric anhydride, 180.

Perthiocarbonic acid, 269.

Perthiocyanic acid, 284.

Perthiocyanic acid, 279.

Perthiocyanogen, 284.

Petate, 350.

"Pharaoh's serpents," 282.

Phosphoric selenide, 342.

Phosphorous selenide, 342.

Phosphorus chloroselenide, 342.

— monoselenide, 342.

— pentaselenide, 342.

— subselenide, 341.

— thioselenides, 342.

— triselenide, 342.

Piperazine tellurate, 288.

Polonium, 3.

Polyselenides, 315.

Polysulphides, Hydrogen, 68-73.

— —, Constitution, 71.

— —, Metallic, 67.

Polythionic acids, 206-224.

— —, Constitution, 221.

— —, Estimation, 223.

Potassium chloropyroselenite, 330.

— dithioformate, 265.

— hexathionate, 220.

— hydrosulphite, 225.

— hydroxylamine disulphonate, 247.

— — trisulphonate, 246.

— oxy-selenophosphate, 343.

— platyselenocyanate, 348.

— pyrosulphate, 99.

— selenate, 336.

— selenibromide, 320.

— selenides, 300.

— selenocyanate, 347.

— selenoxanthate, 344.

— tellurates, 387.

— telluride, 358.

— tellurites, 383.

— tetraselenite, 330.

— tetratellurate, 388.

— thiotellurite, 389.

— xanthate, 268.

"Purple acid," 251.

Pyrosulphates, 147.

Pyrosulphites, 131, 132.

Pyrosulphuric acid, 144-147.

Pyrosulphurous acid, 124.

Pyrosulphuryl chloride, 95-97, 301.

Pyrotellurates, 387.

Pyrotelluryl sulphate, 389.

RADIO-TELLURIUM, 3.

Radium F, 3.

Red sulphur, 8.

Rhodanic acid, 278.

Rongaite, 228, 229.

SELENATES, 336-337.

Selenibromides, 319.

Selenic acid, 331-335.

— —, Hydrates, 333.

— anhydride, 331.

Selenides, Metallic, 300, 313-315.

— —, Organic, 315.

Selenious acid, 328.

Selenites, 330.

Selenito salts, 330.

Selenium, Allotropy of, 289-293.

- , Amorphous, 290, 291.
- , —, Red, 291.
- , Applications, 301, 302.
- , Atomic number, 304.
- , — weight, 303.
- , Behaviour towards light, 297-299.
- , — with iodine, 320.
- , Chemical properties, 299.
- , Colloidal, 293-296.
- , Crystalline, 291-293.
- , —, Grey, 292.
- , —, Red, 291, 292.
- , Detection, 305-307.
- , Discovery, 286.
- , Electrical properties, 297.
- , Estimation, 307-310.
- , — in organic compounds, 308.
- , — — sulphide minerals, 309.
- , — — sulphite-cellulose liquors, 310.
- , — — sulphur, 310.
- , Extraction, 287.
- , Gaseous dissociation, 289.
- , Isotopes, 304.
- , "Liquid," 291.
- , "Metallic," 290, 292.
- , Molecular complexity in solution, 290.
- , — constitution, 305.
- , Monoclinic, 291.
- , Occurrence, 286.
- , Physical properties, 296.
- , Physiological action, 302.
- , Purification, 289.
- , Spectrum, 299.
- , Use in glass industry, 301, 302.
- , Valency, 304.
- , Vapour density, 289.
- , "Vitrous," 290.

Selenium "alums," 337.

- boride, 349.
- chlorotribromide, 320.
- dichloride, 318.
- dichlorodibromide, 320.
- dicyanide, 345.
- dioxide, 326-328.
- —, Additive compounds, 325, 327.
- — monohydrate, 327.
- hexafluoride, 315.
- monobromide, 318.
- monochloride, 316.
- nitride, 340.
- oxybromide, 324.
- oxychloride, 320-324.
- oxyfluoride, 315, 320.
- sulphoxide, 338.
- tetrabromide, 319.
- tetrachloride, 317.
- tetrachlorobromide, 320.
- tetrafluoride, 315.
- trioxide, 331.

Selenocyanates, 346.**Selenocyanic acid, 346.****Selenocyanogen, 345.****Selenonitronic acid, 341.****Selenopentathionic acid, 340.****Selenophosphates, 342.****Selenosulphuric acid, 338.****Selenotritthonates, 339.****Selenotritthionic acid, 339.****Selenyl chloride, 320-324.****Silicon selenide, 348.****Silver selenide, 300.**

— selenocyanate, 348.

— telluryl tartrate, 381.

— thiocyanate, 282.

Sodium formaldehydesulphoxylate, 102, 228.

— hydrosulphite, 225-233.

— monoselenoxanthate, 345.

— perthiocarbonate, 269.

— polytelluride, 358.

— selenate, 336.

— selenides, 300.

— selenocyanate, 348.

— sulphoxylate, 102.

— telluride, 358.

— tellurites, 383.

— thiocarbonate, 266.

— thioselenide, 315.

— thiosulphate, 193-206.

— —, Applications, 202.

— —, Decomposition in aqueous solution, 195.

— —, Preparation, 193.

— —, Properties, 199.

— trioxyselenophosphate, 343.

Strontium oxyselenophosphate, 343.

— selenocyanate, 346.

Sulphamide, 241.**Sulphammonium, 237.****Sulphat-ammon, 244.****Sulphates, 173.****Sulphazilic acid, 251.****Sulphazinic acid, 247.****Sulphazotinic acid, 247.****Sulphenic acids, 101.****Sulphides, Metallic, 61-65.****Sulphimide, 242.****Sulphimic acids, 102.****Sulphites, 130-133.****Sulphocyanic acid, 278.****Sulphones, 100, 102.****Sulphonic acids, 242-251.****Sulphomitronic acid, 154, 251.****Sulphonium salts, 40.****Sulphoxides, 101.****Sulphoxylates, 102, 229.****Sulphoxylic acid, 102, 124.**

— anhydride, 124.

Sulphur I., 20.

— II., 22.

— III., 24.

— IV., 26.

—, α -, 20.—, β -, 22.—, γ -, 20, 21, 27, 28.—, δ -, 30.—, ζ -, 26.—, η -, 26.—, λ -, 16-21.—, μ -, 16-21, 27.—, π -, 17, 20, 21, 29.

Sulphur, 4, 17, 26:

- , Allotropy of, 14-30.
- , Amorphous, Insoluble, 26.
- , —, Soluble, 28.
- , Annual output, 9.
- , Applications, 12.
- , Atomic number, 41.
- , — weight, 40-43.
- , Behaviour with iodine, 84.
- , Black, 8, 29.
- , Blue, 29.
- , Chemical properties of, 36, 37.
- , Chemically pure, 12.
- , Colloidal, 30-32.
- , Detection, 43.
- , Effect of heat on, 15.
- , Engel's rhombohedral, 26.
- , Estimation, 43-45.
- , Extraction, 9, 10.
- , —, Calcarone method, 10.
- , —, Frasch's method, 10.
- , Fertilising action, 13.
- , "Flowers of," 12, 27.
- , History, 8.
- , Isotopes, 41.
- , Liquid, Viscosity of, 15, 18.
- , "Liver of," 28, 52, 68.
- , "Milk of," 28.
- , Molecular complexity, 15, 17, 39.
- , Monoclinic, 22-26.
- , Nacreous, 24.
- , Occurrence, 8.
- , Octahedral, 20.
- , Phase diagram, 24.
- , Physical properties, 32-36.
- , Plastic, 19.
- , Precipitated, 28.
- , Prismatic, 22.
- , Red, 8.
- , Refining, 12.
- , Rhombic, 20.
- , Roll, 12.
- , Spectrum, 35, 36.
- , Sublimed, 12.
- , Tabular, 26.
- , Triclinic, 26.
- , Valency, 39.
- , vapour, Absorption spectrum, 15.
- , —, Density, 15.
- Sulphur chlorides, 74.
- , dichloride, 74, 81.
- , —, Action of ammonia on, 233.
- , dioxide, 103-123.
- , —, Applications, 121.
- , —, Chemical properties, 114-121.
- , —, Constitution, 123.
- , —, Detection, 122.
- , —, Estimation, 122.
- , —, Liquid, 111-114, 122.
- , —, Occurrence, 103.
- , —, Physical properties, 106.
- , —, Physiological action, 121.
- , —, Preparation, 103-106.
- , —, Solid, 114.
- , —, Solubility in sulphuric acid, 110, 111.
- , —, — water, 108.

Sulphur heptoxide, 180.

- , hexafluoride, 73.
- , monobromide, 88.
- , monochloride, 74, 76-81.
- , monofluoride, 73.
- , nitrides, 233-237.
- , oxybromide, 100.
- , oxychlorides, 87-97.
- , oxyfluorides, 84-86.
- , oxytetrachloride, 94.
- , "selenide," 329.
- , -selenium oxytetrachloride, 301, 324.
- , —, sesquioxide, 338.
- , sesquioxide, 224.
- , -tellurium sesquioxide, 357.
- , tetrachloride, 75, 82.
- , tetrafluoride, 73.
- , tetroxide, 180.
- , thiocyanate, 278.
- , trioxide, 135-144.
- , —, α -, 138.
- , —, β -, 138.
- , —, Chemical properties, 141-143.
- , —, Constitution, 143.
- , —, Formation, 136.
- , —, History, 135.
- , —, Modifications, 138-141.
- , —, Physical properties, 138.
- , —, Preparation, 136.
- Sulphuretted hydrogen, 47.
- Sulphuric acid, 148-179.
- , —, Annual output, 149.
- , —, Applications, 172.
- , —, Behaviour towards water, 164-169.
- , —, Chemical properties, 170.
- , —, Concentration, 156, 157.
- , —, —, Gaillard plant, 157.
- , —, Constitution, 175-177.
- , —, "Contact" process, 159-162.
- , —, Detection, 177.
- , —, Electrolysis, 169.
- , —, Estimation, 177-179.
- , —, Formation, 148.
- , —, Fuming, 144-147.
- , —, History, 148, 149.
- , —, Hydrates, 167-169.
- , —, Ionisation, 169.
- , —, "Lead chamber" process, 149-156.
- , —, —, Gay-Lussac tower, 152.
- , —, —, Glover tower, 150, 287, 288.
- , —, —, Pyrites burners, 150.
- , —, —, Theory of, 153.
- , —, Manufacture, 149-162.
- , —, —, Modern tendencies, 162.
- , —, Nordhausen, 144.
- , —, Occurrence, 148.
- , —, Physical properties, 162.
- , —, Pure, 163.
- , —, Purification, 158.
- Sulphurous acid, 123-135.
- , —, Auto-reduction of, 125.
- , —, Autoxidation of, 124.
- , —, Constitution, 133.
- , —, Detection, 128.
- , —, Estimation, 128-130.

Sulphurous acid, Formation, 123.
 — —, Properties, 123-128.
 — —, Reducing action, 126.
Sulphuryl chloride, 91-94.
 — fluoride, 85.
Sylvanite, 350.

TELLURATES, 387.
 — —, Complex, 388.
 — —, Organic, 388.
Telluribromides, 377.
Telluric acid, Estimation, 367.
 — acids, 384-387.
Tellurichlorides, 375.
Tellurides, Metallic, 350, 358, 371, 372.
 — —, Organic, 372.
Telluri-iodides, 378.
Tellurite, 350, 380.
Tellurites, 382, 383.
Tellurium, Allotropic forms, 353.
 — —, Alloys, 363.
 — —, Amorphous, 353.
 — —, Atomic number, 361, 363.
 — —, — weight, 360-363.
 — —, Chemical properties, 357, 369.
 — —, Colloidal, 355.
 — —, Crystalline, 353.
 — —, Detection, 364.
 — —, Estimation, Electrolytic, 366.
 — —, —, Gravimetric, 365.
 — —, —, Volumetric, 367.
 — —, Extraction, 351.
 — —, Fluorescence of vapour, 356.
 — —, High-frequency spectrum, 361.
 — —, History, 351.
 — —, Isotopes, 363.
 — —, Liquid, 354.
 — —, Occurrence, 350.
 — —, Physical properties, 352.
 — —, Physiological action, 359.
 — —, Position in Periodic Table, 360, 369.
 — —, Purification, 352.
 — —, Spectrum, 356.
Tellurium dibromide, 376.
 — dichloride, 373.
 — dicyanide, 391.
 — di-iodide, 378.
 — dioxide, 379.
 — —, Acidic properties, 382.
 — —, Basic properties, 381.
 — disulphate, 389.
 — disulphide, 388.
 — hexafluoride, 373.
 — monoxide, 379.
 — nitrate, Basic, 379, 390.
 — nitride, 390.
 — nitrite, 357, 390.
 — oxybromides, 377.
 — oxychloride, 376.
 — oxyfluorides, 373.
 — perchlorate, 376.
 — selenate, Basic, 390.
 — -selenium sesquioxide, 357, 390.
 — suboxide, 379.
 — sulphates, 389.
 — sulphoxide, 224, 389.

Tellurium-sulphur sesquioxide, 357, 379, 389.
 — tartrates, 381.
 — tetrabromide, 376.
 — tetrachloride, 374.
 — —, Additive compounds, 375, 376.
 — tetrafluoride, 372.
 — tetra-iodide, 378.
 — trioxide, 383.
 — trisulphide, 389.
*cyclo*Telluropentane-3 : 5-diones, 360.
Telluropentathionic acid, 390.
Tellurous acid, 382.
 — —, Estimation, 367.
Tetradymite, 350, 366.
Tetramethylthioethylene, 268.
Tetraphosphorus di-iodide triselenide, 320.
 — triselenide, 342.
Tetratellurates, 387.
Tetratellurous acid, 382.
Tetrathionates, 213-217.
Tetrathionic acid, 213-217.
 — —, Constitution, 221.
 — —, Estimation, 223.
 — —, Preparation, 213.
 — —, Properties, 215.
Thallium selenides, 314.
Thiocarbamide, 274.
 — tellurate, 388.
Thiocarbonates, 266-268.
Thiocarbonic acid, 266, 274.
Thiocarbonyl chloride, 272.
 — sulphochloride, 273.
 — tetrachloride, 273.
Thiocyanates, 280-284
 — —, Complex, 283.
Thiocyanic acid, 278.
 — thioanhydride, 277.
Thiocyanogen, 276, 277.
 "Thiocyanoselenous acid," 330.
Thiodithiazyl dichloride, 239.
Thioformaldehyde, 265.
Thiolecarbonic acid, 266, 268.
Thioalthioncarbamic acid, 274.
Thioalthioncarbamic acid, 266.
Thioncarbamic acid, 266.
Thionylamide, 241.
Thionyl bromide, 100.
 — chloride, 87-91.
 — fluoride, 84.
Thiophen, 258, 262.
Thiophosgene, 272.
Thiophten, 258.
Thioselenic acid, 338.
Thiosulphates, 192-206.
 — —, Applications, 202.
 — —, Constitution, 203.
 — —, Decomposition, 195.
 — —, Detection, 204.
 — —, Estimation, 204-206.
 — —, Formation, 193.
 — —, Properties, 199.
Thiosulphuric acid, 192-206.
 — —, Constitution, 202.
 — —, Decomposition, 195.
 — —, Formation, 193.

Thiosulphuric acid, Properties, 194.

Thiotellurites, 369.

Thiotrithiazyl bromide, 240.

— chloride, 238.

— compounds, Constitution, 240.

— hydrogen sulphate, 240.

— iodide, 240.

— nitrate, 238, 240.

— thiocyanate, 240.

Thiourea, 274.

Thiourethane, 268.

Tolueneseleninic acid, 333.

Triammonium imidodisulphinate, 120, 243.

Trichloromethyl disulphide, 272, 273.

— sulphur chloride, 272, 273.

— trisulphide, 272, 273.

Trisulphimide, 242.

Trisulphur tetrachloride, 74.

Trithiazyl chloride, 238.

Trithiocyanuric acid, 284.

Trithionates, 210-213.

Trithionic acid, 210-213.

— —, Constitution, 221.

— —, Estimation, 223.

— —, Preparation, 210.

— —, Properties, 211.

ULTRAMARINE, 29.

Uranyl selenites, 330.

VANADOSELENITES, 330.

"Violet acid," 154, 262.

Viscose, 264.

Vulcanisation, 13, 264.

WACKENRODER'S solution, 217, 220.

Water, Heat of formation, 5.

XANTHATES, 264, 268.

Xanthic acid, 268.

Xanthogenamide, 268.

Xanthogenic acid, 268.

Zinc hydrosulphite, 225.

— selenide, 314.

— selenocyanate, 348.

— sulphonylate, 102.

— xanthates, 264.

Zorgite, 286.

